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Chemical Nomenclature

By the end of this module, you will be able to:

- Derive names for common types of inorganic compounds using a systematic approach

Nomenclature, a collection of rules for naming things, is important in science and in many other situations. This module describes an approach that is used to name simple ionic and molecular compounds, such as NaCl, CaCO₃, and N₂O₄. The simplest of these are **binary compounds**, those containing only two elements, but we will also consider how to name ionic compounds containing polyatomic ions, and one specific, very important class of compounds known as acids (subsequent chapters in this text will focus on these compounds in great detail). We will limit our attention here to inorganic compounds, compounds that are composed principally of elements other than carbon, and will follow the nomenclature guidelines proposed by IUPAC. The rules for organic compounds, in which carbon is the principle element, will be treated in a later chapter on organic chemistry.

Ionic Compounds

To name an inorganic compound, we need to consider the answers to several questions. First, is the compound ionic or molecular? If the compound is ionic, does the metal form ions of only one type (fixed charge) or more than one type (variable charge)? Are the ions monatomic or polyatomic? If the compound is molecular, does it contain hydrogen? If so, does it also contain oxygen? From the answers we derive, we place the compound in an appropriate category and then name it accordingly.

Compounds Containing Only Monatomic Ions

The name of a binary compound containing monatomic ions consists of the name of the cation (the name of the metal) followed by the name of the anion (the name of the nonmetallic element with its ending replaced by the suffix *-ide*). Some examples are given in [\[link\]](#).

Names of Some Ionic Compounds	
NaCl, sodium chloride	Na ₂ O, sodium oxide
KBr, potassium bromide	CdS, cadmium sulfide
CaI ₂ , calcium iodide	Mg ₃ N ₂ , magnesium nitride
CsF, cesium fluoride	Ca ₃ P ₂ , calcium phosphide
LiCl, lithium chloride	Al ₄ C ₃ , aluminum carbide

Compounds Containing Polyatomic Ions

Compounds containing polyatomic ions are named similarly to those containing only monatomic ions, i.e. by naming first the cation and then the anion. Examples are shown in [\[link\]](#).

Names of Some Polyatomic Ionic Compounds	
KC ₂ H ₃ O ₂ , potassium acetate	NH ₄ Cl, ammonium chloride
NaHCO ₃ , sodium bicarbonate	CaSO ₄ , calcium sulfate
Al ₂ (CO ₃) ₃ , aluminum carbonate	Mg ₃ (PO ₄) ₂ , magnesium phosphate

Note:

Ionic Compounds in Your Cabinets

Every day you encounter and use a large number of ionic compounds. Some of these compounds, where they are found, and what they are used for are listed in [\[link\]](#). Look at the label or ingredients list on the various products that you use during the next few days, and see if you run into any of those in this table, or find other ionic compounds that you could now name or write as a formula.

Everyday Ionic Compounds

Ionic Compound	Use
NaCl, sodium chloride	ordinary table salt
KI, potassium iodide	added to “iodized” salt for thyroid health
NaF, sodium fluoride	ingredient in toothpaste
NaHCO ₃ , sodium bicarbonate	baking soda; used in cooking (and as antacid)
Na ₂ CO ₃ , sodium carbonate	washing soda; used in cleaning agents
NaOCl, sodium hypochlorite	active ingredient in household bleach
CaCO ₃ calcium carbonate	ingredient in antacids
Mg(OH) ₂ , magnesium hydroxide	ingredient in antacids

Everyday Ionic Compounds	
Ionic Compound	Use
$\text{Al}(\text{OH})_3$, aluminum hydroxide	ingredient in antacids
NaOH , sodium hydroxide	lye; used as drain cleaner
K_3PO_4 , potassium phosphate	food additive (many purposes)
MgSO_4 , magnesium sulfate	added to purified water
Na_2HPO_4 , sodium hydrogen phosphate	anti-caking agent; used in powdered products
Na_2SO_3 , sodium sulfite	preservative

Compounds Containing a Metal Ion with a Variable Charge

Most of the transition metals can form two or more cations with different charges. Compounds of these metals with nonmetals are named with the same method as compounds in the first category, except the charge of the metal ion is specified by a Roman numeral in parentheses after the name of the metal. The charge of the metal ion is determined from the formula of the compound and the charge of the anion. For example, consider binary ionic compounds of iron and chlorine. Iron typically exhibits a charge of either $2+$ or $3+$ (see [\[link\]](#)), and the two corresponding compound formulas are FeCl_2 and FeCl_3 . The simplest name, “iron chloride,” will, in this case, be ambiguous, as it does not distinguish between these two compounds. In cases like this, the charge of the metal ion is included as a Roman numeral in parentheses immediately following the metal name. These two compounds are then unambiguously named iron(II) chloride and iron(III) chloride, respectively. Other examples are provided in [\[link\]](#).

Names of Some Transition Metal Ionic Compounds	
Transition Metal Ionic Compound	Name
FeCl_3	iron(III) chloride
Hg_2O	mercury(I) oxide
HgO	mercury(II) oxide
$\text{Cu}_3(\text{PO}_4)_2$	copper(II) phosphate

Out-of-date nomenclature used the suffixes *-ic* and *-ous* to designate metals with higher and lower charges, respectively: Iron(III) chloride, FeCl_3 , was previously called ferric chloride, and iron(II) chloride, FeCl_2 , was known as ferrous chloride. Though this naming convention has been largely abandoned by the scientific community, it remains in use by some segments of industry. For example, you may see the words *stannous fluoride* on a tube of toothpaste. This represents the formula SnF_2 , which is more properly named tin(II) fluoride. The other fluoride of tin is SnF_4 , which was previously called stannic fluoride but is now named tin(IV) fluoride.

Example:

Naming Ionic Compounds

Name the following ionic compounds, which contain a metal that can have more than one ionic charge:

- (a) Fe_2S_3
- (b) CuSe
- (c) GaN
- (d) CrCl_3
- (e) $\text{Ti}_2(\text{SO}_4)_3$

Solution

The anions in these compounds have a fixed negative charge (S^{2-} , Se^{2-} , N^{3-} , Cl^- , and SO_4^{2-}), and the compounds must be neutral. Because the

total number of positive charges in each compound must equal the total number of negative charges, the positive ions must be Fe^{3+} , Cu^{2+} , Ga^{3+} , Cr^{3+} , and Ti^{3+} . These charges are used in the names of the metal ions:

- (a) iron(III) sulfide
- (b) copper(II) selenide
- (c) gallium(III) nitride
- (d) chromium(III) chloride
- (e) titanium(III) sulfate

Check Your Learning

Write the formulas of the following ionic compounds:

- (a) chromium(III) phosphide
- (b) mercury(II) sulfide
- (c) manganese(II) phosphate
- (d) copper(I) oxide
- (e) chromium(VI) fluoride

Note:

Answer:

(a) CrP ; (b) HgS ; (c) $\text{Mn}_3(\text{PO}_4)_2$; (d) Cu_2O ; (e) CrF_6

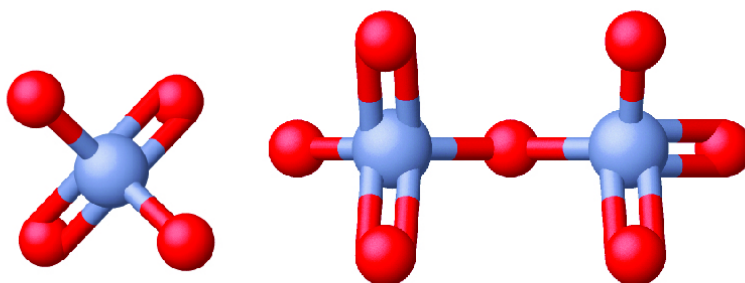
Note:

Erin Brokovich and Chromium Contamination

In the early 1990s, legal file clerk Erin Brockovich ([\[link\]](#)) discovered a high rate of serious illnesses in the small town of Hinckley, California. Her investigation eventually linked the illnesses to groundwater contaminated by Cr(VI) used by Pacific Gas & Electric (PG&E) to fight corrosion in a nearby natural gas pipeline. As dramatized in the film *Erin Brokovich* (for which Julia Roberts won an Oscar), Erin and lawyer Edward Masry sued PG&E for contaminating the water near Hinckley in 1993. The settlement they won in 1996—\$333 million—was the largest amount ever awarded for a direct-action lawsuit in the US at that time.



(a)



(b)

(a) Erin Brockovich found that Cr(VI), used by PG&E, had contaminated the Hinckley, California, water supply. (b) The Cr(VI) ion is often present in water as the polyatomic ions chromate, CrO_4^{2-} (left), and dichromate, $\text{Cr}_2\text{O}_7^{2-}$ (right).

Chromium compounds are widely used in industry, such as for chrome plating, in dye-making, as preservatives, and to prevent corrosion in cooling tower water, as occurred near Hinckley. In the environment, chromium exists primarily in either the Cr(III) or Cr(VI) forms. Cr(III), an ingredient of many vitamin and nutritional supplements, forms compounds that are not very soluble in water, and it has low toxicity. But Cr(VI) is much more toxic and forms compounds that are reasonably soluble in water. Exposure to small amounts of Cr(VI) can lead to damage of the respiratory, gastrointestinal, and immune systems, as well as the kidneys, liver, blood, and skin.

Despite cleanup efforts, Cr(VI) groundwater contamination remains a problem in Hinckley and other locations across the globe. A 2010 study by the Environmental Working Group found that of 35 US cities tested, 31 had higher levels of Cr(VI) in their tap water than the public health goal of 0.02 parts per billion set by the California Environmental Protection Agency.

Molecular (Covalent) Compounds

The bonding characteristics of inorganic molecular compounds are different from ionic compounds, and they are named using a different system as well. The charges of cations and anions dictate their ratios in ionic compounds, so specifying the names of the ions provides sufficient information to determine chemical formulas. However, because covalent bonding allows for significant variation in the combination ratios of the atoms in a molecule, the names for molecular compounds must explicitly identify these ratios.

Compounds Composed of Two Elements

When two nonmetallic elements form a molecular compound, several combination ratios are often possible. For example, carbon and oxygen can form the compounds CO and CO₂. Since these are different substances with different properties, they cannot both have the same name (they cannot both be called carbon oxide). To deal with this situation, we use a naming method that is somewhat similar to that used for ionic compounds, but with added prefixes to specify the numbers of atoms of each element. The name of the more metallic element (the one farther to the left and/or bottom of the periodic table) is first, followed by the name of the more nonmetallic element (the one farther to the right and/or top) with its ending changed to the suffix *-ide*. The numbers of atoms of each element are designated by the Greek prefixes shown in [\[link\]](#).

Nomenclature Prefixes				
Number	Prefix		Number	Prefix
1 (sometimes omitted)	mono-		6	hexa-
2	di-		7	hepta-

Nomenclature Prefixes				
Number	Prefix		Number	Prefix
3	tri-		8	octa-
4	tetra-		9	nona-
5	penta-		10	deca-

When only one atom of the first element is present, the prefix *mono-* is usually deleted from that part. Thus, CO is named carbon monoxide, and CO₂ is called carbon dioxide. When two vowels are adjacent, the *a* in the Greek prefix is usually dropped. Some other examples are shown in [\[link\]](#).

Names of Some Molecular Compounds Composed of Two Elements				
Compound	Name		Compound	Name
SO ₂	sulfur dioxide		BCl ₃	boron trichloride
SO ₃	sulfur trioxide		SF ₆	sulfur hexafluoride
NO ₂	nitrogen dioxide		PF ₅	phosphorus pentafluoride
N ₂ O ₄	dinitrogen tetroxide		P ₄ O ₁₀	tetraphosphorus decaoxide

Names of Some Molecular Compounds Composed of Two Elements				
Compound	Name		Compound	Name
N_2O_5	dinitrogen pentoxide		IF_7	iodine heptafluoride

There are a few common names that you will encounter as you continue your study of chemistry. For example, although NO is often called nitric oxide, its proper name is nitrogen monoxide. Similarly, N_2O is known as nitrous oxide even though our rules would specify the name dinitrogen monoxide. (And H_2O is usually called water, not dihydrogen monoxide.) You should commit to memory the common names of compounds as you encounter them.

Example:

Naming Covalent Compounds

Name the following covalent compounds:

- (a) SF_6
- (b) N_2O_3
- (c) Cl_2O_7
- (d) P_4O_6

Solution

Because these compounds consist solely of nonmetals, we use prefixes to designate the number of atoms of each element:

- (a) sulfur hexafluoride
- (b) dinitrogen trioxide
- (c) dichlorine heptoxide
- (d) tetraphosphorus hexoxide

Check Your Learning

Write the formulas for the following compounds:

- (a) phosphorus pentachloride
- (b) dinitrogen monoxide
- (c) iodine heptafluoride
- (d) carbon tetrachloride

Note:

Answer:

(a) PCl_5 ; (b) N_2O ; (c) IF_7 ; (d) CCl_4

Note:



The following [website](#) provides practice with naming chemical compounds and writing chemical formulas. You can choose binary, polyatomic, and variable charge ionic compounds, as well as molecular compounds.

Binary Acids

Some compounds containing hydrogen are members of an important class of substances known as acids. The chemistry of these compounds is explored in more detail in later chapters of this text, but for now, it will suffice to note that many acids release hydrogen ions, H^+ , when dissolved in water. To denote this distinct chemical property, a mixture of water with an acid is given a name derived from the compound's name. If the compound is a **binary acid** (comprised of hydrogen and one other nonmetallic element):

1. The word "hydrogen" is changed to the prefix *hydro-*
2. The other nonmetallic element name is modified by adding the suffix *-ic*
3. The word "acid" is added as a second word

For example, when the gas HCl (hydrogen chloride) is dissolved in water, the solution is called *hydrochloric acid*. Several other examples of this nomenclature are shown in [\[link\]](#).

Names of Some Simple Acids	
Name of Gas	Name of Acid
HF(<i>g</i>), hydrogen fluoride	HF(<i>aq</i>), hydrofluoric acid
HCl(<i>g</i>), hydrogen chloride	HCl(<i>aq</i>), hydrochloric acid
HBr(<i>g</i>), hydrogen bromide	HBr(<i>aq</i>), hydrobromic acid
HI(<i>g</i>), hydrogen iodide	HI(<i>aq</i>), hydroiodic acid
H ₂ S(<i>g</i>), hydrogen sulfide	H ₂ S(<i>aq</i>), hydrosulfuric acid

Oxyacids

Many compounds containing three or more elements (such as organic compounds or coordination compounds) are subject to specialized nomenclature rules that you will learn later. However, we will briefly discuss the important compounds known as **oxyacids**, compounds that contain hydrogen, oxygen, and at least one other element, and are bonded in such a way as to impart acidic properties to the compound (you will learn the details of this in a later chapter). Typical oxyacids consist of hydrogen combined with a polyatomic, oxygen-containing ion. To name oxyacids:

1. Omit “hydrogen”
2. Start with the root name of the anion

3. Replace *–ate* with *–ic*, or *–ite* with *–ous*
4. Add “acid”

For example, consider H_2CO_3 (which you might be tempted to call “hydrogen carbonate”). To name this correctly, “hydrogen” is omitted; the *–ate* of carbonate is replaced with *–ic*; and acid is added—so its name is carbonic acid. Other examples are given in [\[link\]](#). There are some exceptions to the general naming method (e.g., H_2SO_4 is called sulfuric acid, not sulfic acid, and H_2SO_3 is sulfurous, not sulfous, acid).

Names of Common Oxyacids		
Formula	Anion Name	Acid Name
$\text{HC}_2\text{H}_3\text{O}_2$	acetate	acetic acid
HNO_3	nitrate	nitric acid
HNO_2	nitrite	nitrous acid
HClO_4	perchlorate	perchloric acid
H_2CO_3	carbonate	carbonic acid
H_2SO_4	sulfate	sulfuric acid
H_2SO_3	sulfite	sulfurous acid
H_3PO_4	phosphate	phosphoric acid

Key Concepts and Summary

Chemists use nomenclature rules to clearly name compounds. Ionic and molecular compounds are named using somewhat-different methods. Binary ionic compounds typically consist of a metal and a nonmetal. The name of the metal is written first, followed by the name of the nonmetal with its ending changed to *-ide*. For example, K_2O is called potassium oxide. If the metal can form ions with different charges, a Roman numeral in parentheses follows the name of the metal to specify its charge. Thus, FeCl_2 is iron(II) chloride and FeCl_3 is iron(III) chloride. Some compounds contain polyatomic ions; the names of common polyatomic ions should be memorized. Molecular compounds can form compounds with different ratios of their elements, so prefixes are used to specify the numbers of atoms of each element in a molecule of the compound. Examples include SF_6 , sulfur hexafluoride, and N_2O_4 , dinitrogen tetroxide. Acids are an important class of compounds containing hydrogen and having special nomenclature rules. Binary acids are named using the prefix *hydro-*, changing the *-ide* suffix to *-ic*, and adding “acid;” HCl is hydrochloric acid. Oxyacids are named by changing the ending of the anion (*-ate* to *-ic* and *-ite* to *-ous*), and adding “acid;” H_2CO_3 is carbonic acid.

Chemistry End of Chapter Exercises

Exercise:

Problem: Name the following compounds:

- (a) CsCl
- (b) BaO
- (c) K_2S
- (d) BeCl_2
- (e) HBr
- (f) AlF_3

Solution:

(a) cesium chloride; (b) barium oxide; (c) potassium sulfide; (d) beryllium chloride; (e) hydrogen bromide; (f) aluminum fluoride

Exercise:

Problem: Name the following compounds:

- (a) NaF
- (b) Rb₂O
- (c) BCl₃
- (d) H₂Se
- (e) P₄O₆
- (f) ICl₃

Exercise:

Problem: Write the formulas of the following compounds:

- (a) rubidium bromide
- (b) magnesium selenide
- (c) sodium oxide
- (d) calcium chloride
- (e) hydrogen fluoride
- (f) gallium phosphide
- (g) aluminum bromide

(h) ammonium sulfate

Solution:

(a) RbBr; (b) MgSe; (c) Na₂O; (d) CaCl₂; (e) HF; (f) GaP; (g) AlBr₃;
(h) (NH₄)₂SO₄

Exercise:

Problem: Write the formulas of the following compounds:

- (a) lithium carbonate
- (b) sodium perchlorate
- (c) barium hydroxide
- (d) ammonium carbonate
- (e) sulfuric acid
- (f) calcium acetate
- (g) magnesium phosphate
- (h) sodium sulfite

Exercise:

Problem: Write the formulas of the following compounds:

- (a) chlorine dioxide
- (b) dinitrogen tetroxide
- (c) potassium phosphide
- (d) silver(I) sulfide
- (e) aluminum nitride

(f) silicon dioxide

Solution:

(a) ClO_2 ; (b) N_2O_4 ; (c) K_3P ; (d) Ag_2S ; (e) AlN ; (f) SiO_2

Exercise:

Problem: Write the formulas of the following compounds:

- (a) barium chloride
- (b) magnesium nitride
- (c) sulfur dioxide
- (d) nitrogen trichloride
- (e) dinitrogen trioxide
- (f) tin(IV) chloride

Exercise:

Problem:

Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:

- (a) Cr_2O_3
 - (b) FeCl_2
 - (c) CrO_3
 - (d) TiCl_4
 - (e) CoO
 - (f) MoS_2
-

Solution:

(a) chromium(III) oxide; (b) iron(II) chloride; (c) chromium(VI) oxide;
(d) titanium(IV) chloride; (e) cobalt(II) oxide; (f) molybdenum(IV)
sulfide

Exercise:**Problem:**

Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:

- (a) NiCO_3
- (b) MoO_3
- (c) $\text{Co}(\text{NO}_3)_2$
- (d) V_2O_5
- (e) MnO_2
- (f) Fe_2O_3

Exercise:**Problem:**

The following ionic compounds are found in common household products. Write the formulas for each compound:

- (a) potassium phosphate
- (b) copper(II) sulfate
- (c) calcium chloride
- (d) titanium(IV) oxide
- (e) ammonium nitrate

(f) sodium bisulfate (the common name for sodium hydrogen sulfate)

Solution:

(a) K_3PO_4 ; (b) CuSO_4 ; (c) CaCl_2 ; (d) TiO_2 ; (e) NH_4NO_3 ; (f) NaHSO_4

Exercise:

Problem:

The following ionic compounds are found in common household products. Name each of the compounds:

(a) $\text{Ca}(\text{H}_2\text{PO}_4)_2$

(b) FeSO_4

(c) CaCO_3

(d) MgO

(e) NaNO_2

(f) KI

Exercise:

Problem: What are the IUPAC names of the following compounds?

(a) manganese dioxide

(b) mercurous chloride (Hg_2Cl_2)

(c) ferric nitrate [$\text{Fe}(\text{NO}_3)_3$]

(d) titanium tetrachloride

(e) cupric bromide (CuBr_2)

Solution:

(a) manganese(IV) oxide; (b) mercury(I) chloride; (c) iron(III) nitrate;
(d) titanium(IV) chloride; (e) copper(II) bromide

Glossary

binary acid

compound that contains hydrogen and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

binary compound

compound containing two different elements.

nomenclature

system of rules for naming objects of interest

oxyacid

compound that contains hydrogen, oxygen, and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

Formula Mass and the Mole Concept

By the end of this section, you will be able to:

- Calculate formula masses for covalent and ionic compounds
- Define the amount unit mole and the related quantity Avogadro's number Explain the relation between mass, moles, and numbers of atoms or molecules, and perform calculations deriving these quantities from one another

We can argue that modern chemical science began when scientists started exploring the quantitative as well as the qualitative aspects of chemistry. For example, Dalton's atomic theory was an attempt to explain the results of measurements that allowed him to calculate the relative masses of elements combined in various compounds. Understanding the relationship between the masses of atoms and the chemical formulas of compounds allows us to quantitatively describe the composition of substances.

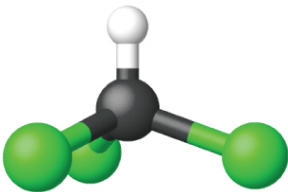
Formula Mass

In an earlier chapter, we described the development of the atomic mass unit, the concept of average atomic masses, and the use of chemical formulas to represent the elemental makeup of substances. These ideas can be extended to calculate the **formula mass** of a substance by summing the average atomic masses of all the atoms represented in the substance's formula.

Formula Mass for Covalent Substances

For covalent substances, the formula represents the numbers and types of atoms composing a single molecule of the substance; therefore, the formula mass may be correctly referred to as a molecular mass. Consider chloroform (CHCl_3), a covalent compound once used as a surgical anesthetic and now primarily used in the production of tetrafluoroethylene, the building block for the "anti-stick" polymer, Teflon. The molecular formula of chloroform indicates that a single molecule contains one carbon atom, one hydrogen atom, and three chlorine atoms. The average molecular mass of a chloroform molecule is therefore equal to the sum of the average atomic masses of these atoms. [\[link\]](#) outlines the calculations used to derive the molecular mass of chloroform, which is 119.37 amu.

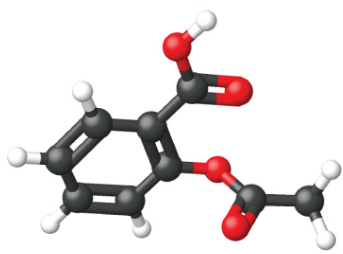
Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	1	×	12.01	=	12.01
H	1	×	1.008	=	1.008
Cl	3	×	35.45	=	106.35
Molecular mass					119.37



The average mass of a chloroform molecule, CHCl_3 , is 119.37 amu, which is the sum of the average atomic masses of each of its constituent atoms. The model shows the molecular structure of chloroform.

Likewise, the molecular mass of an aspirin molecule, $\text{C}_9\text{H}_8\text{O}_4$, is the sum of the atomic masses of nine carbon atoms, eight hydrogen atoms, and four oxygen atoms, which amounts to 180.15 amu ([link](#)).

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	9	×	12.01	=	108.09
H	8	×	1.008	=	8.064
O	4	×	16.00	=	64.00
Molecular mass					180.15



The average mass of an aspirin molecule is 180.15 amu. The model shows the molecular structure of aspirin, $\text{C}_9\text{H}_8\text{O}_4$.

Example:

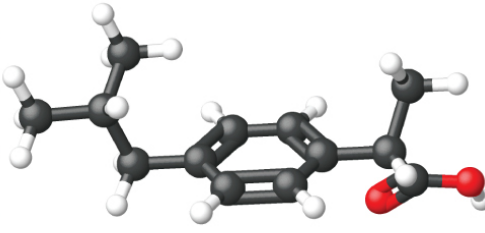
Computing Molecular Mass for a Covalent Compound

Ibuprofen, $\text{C}_{13}\text{H}_{18}\text{O}_2$, is a covalent compound and the active ingredient in several popular nonprescription pain medications, such as Advil and Motrin. What is the molecular mass (amu) for this compound?

Solution

Molecules of this compound are comprised of 13 carbon atoms, 18 hydrogen atoms, and 2 oxygen atoms. Following the approach described above, the average molecular mass for this compound is therefore:

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	13	×	12.01	=	156.13
H	18	×	1.008	=	18.144
O	2	×	16.00	=	32.00
Molecular mass					206.27



Check Your Learning

Acetaminophen, $\text{C}_8\text{H}_9\text{NO}_2$, is a covalent compound and the active ingredient in several popular nonprescription pain medications, such as Tylenol. What is the molecular mass (amu) for this compound?

Note:

Answer:

151.16 amu

Formula Mass for Ionic Compounds

Ionic compounds are composed of discrete cations and anions combined in ratios to yield electrically neutral bulk matter. The formula mass for an ionic compound is calculated in the same way as the formula mass for covalent compounds: by summing the average atomic masses of all the atoms in the compound's formula. Keep in mind, however, that the formula for an ionic compound does not represent the composition of a discrete molecule, so it may not correctly be referred to as the "molecular mass."

As an example, consider sodium chloride, NaCl , the chemical name for common table salt. Sodium chloride is an ionic compound composed of sodium cations, Na^+ , and chloride anions, Cl^- , combined in a 1:1 ratio. The formula mass for this compound is computed as 58.44 amu (see [\[link\]](#)).

Element	Quantity		Average atomic mass (amu)		Subtotal
Na	1	×	22.99	=	22.99
Cl	1	×	35.45	=	35.45
Formula mass					58.44

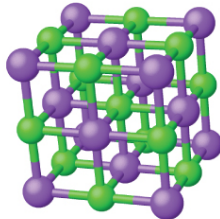


Table salt, NaCl, contains an array of sodium and chloride ions combined in a 1:1 ratio. Its formula mass is 58.44 amu.

Note that the average masses of neutral sodium and chlorine atoms were used in this computation, rather than the masses for sodium cations and chloride anions. This approach is perfectly acceptable when computing the formula mass of an ionic compound. Even though a sodium cation has a slightly smaller mass than a sodium atom (since it is missing an electron), this difference will be offset by the fact that a chloride anion is slightly more massive than a chloride atom (due to the extra electron). Moreover, the mass of an electron is negligibly small with respect to the mass of a typical atom. Even when calculating the mass of an isolated ion, the missing or additional electrons can generally be ignored, since their contribution to the overall mass is negligible, reflected only in the nonsignificant digits that will be lost when the computed mass is properly rounded. The few exceptions to this guideline are very light ions derived from elements with precisely known atomic masses.

Example:

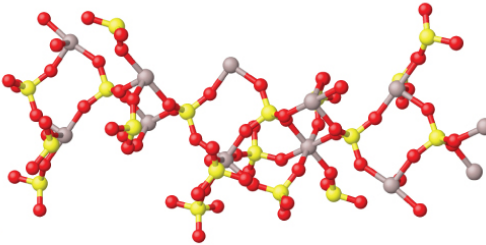
Computing Formula Mass for an Ionic Compound

Aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$, is an ionic compound that is used in the manufacture of paper and in various water purification processes. What is the formula mass (amu) of this compound?

Solution

The formula for this compound indicates it contains Al^{3+} and SO_4^{2-} ions combined in a 2:3 ratio. For purposes of computing a formula mass, it is helpful to rewrite the formula in the simpler format, $\text{Al}_2\text{S}_3\text{O}_{12}$. Following the approach outlined above, the formula mass for this compound is calculated as follows:

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
Al	2	×	26.98	=	53.96
S	3	×	32.06	=	96.18
O	12	×	16.00	=	192.00
Molecular mass					342.14



Check Your Learning

Calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, is an ionic compound and a common anti-caking agent added to food products. What is the formula mass (amu) of calcium phosphate?

Note:

Answer:

310.18 amu

The Mole

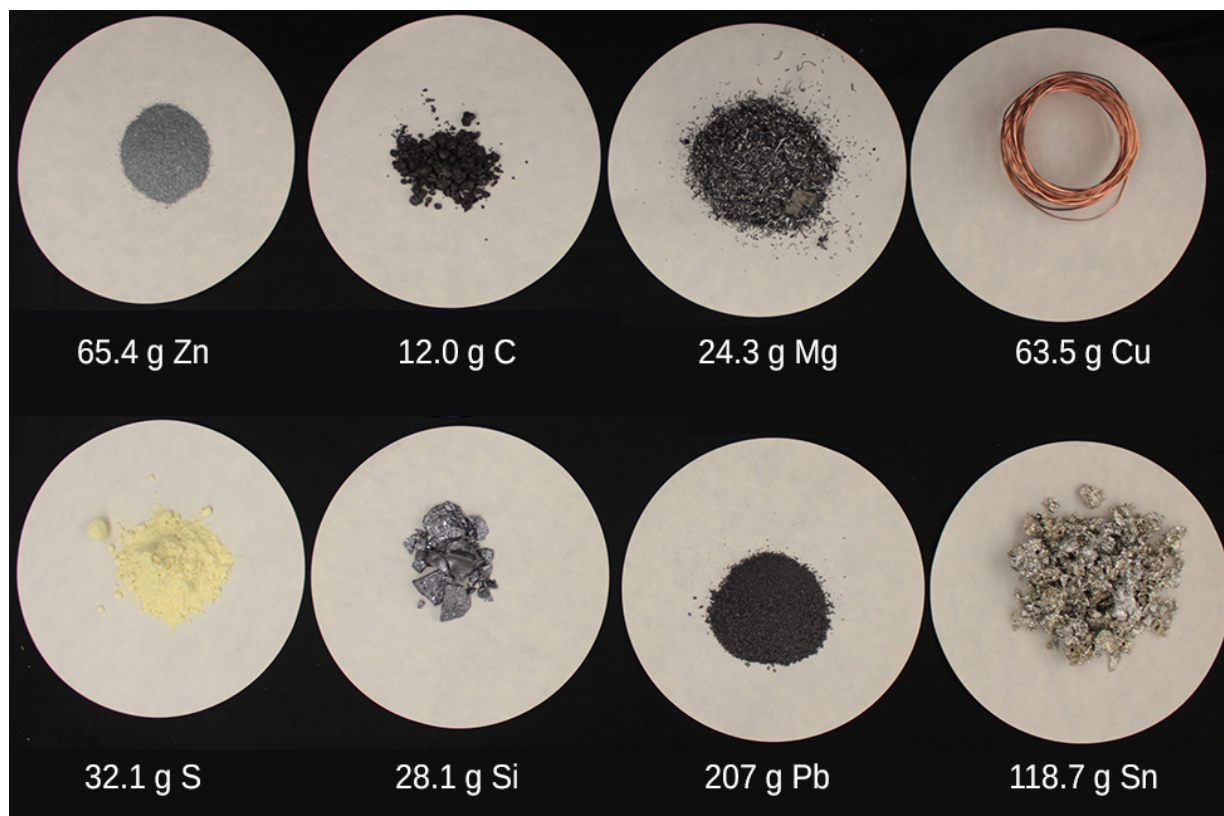
The identity of a substance is defined not only by the types of atoms or ions it contains, but by the quantity of each type of atom or ion. For example, water, H_2O , and hydrogen peroxide, H_2O_2 , are alike in that their respective molecules are composed of hydrogen and oxygen atoms. However, because a hydrogen peroxide molecule contains two oxygen atoms, as opposed to the water molecule, which has only one, the two substances exhibit very different properties. Today, we possess sophisticated instruments that allow the direct measurement of these defining microscopic traits; however, the same traits were originally derived from the measurement of macroscopic properties (the masses and volumes of bulk quantities of matter) using relatively simple tools (balances and volumetric glassware). This experimental approach required the introduction of a new unit for amount of substances, the *mole*, which remains indispensable in modern chemical science.

The mole is an amount unit similar to familiar units like pair, dozen, gross, etc. It provides a specific measure of *the number* of atoms or molecules in a bulk sample of matter. A **mole** is defined as the amount of substance containing the same number of discrete entities (such as atoms, molecules, and ions) as the number of atoms in a sample of pure ^{12}C weighing exactly 12 g. One Latin connotation for the word “mole” is “large mass” or “bulk,” which is consistent with its use as the name for this unit. The mole provides a link between an easily measured macroscopic property, bulk mass, and an extremely important fundamental property, number of atoms, molecules, and so forth.

The number of entities composing a mole has been experimentally determined to be $6.02214179 \times 10^{23}$, a fundamental constant named **Avogadro's number (N_A)** or the Avogadro constant in honor of Italian scientist Amedeo Avogadro. This constant is properly reported with an explicit unit of “per mole,” a conveniently rounded version being $6.022 \times 10^{23}/\text{mol}$.

Consistent with its definition as an amount unit, 1 mole of any element contains the same number of atoms as 1 mole of any other element. The masses of 1 mole of different elements, however, are different, since the masses of the individual atoms are drastically different. The

molar mass of an element (or compound) is the mass in grams of 1 mole of that substance, a property expressed in units of grams per mole (g/mol) (see [\[link\]](#)).



Each sample contains 6.022×10^{23} atoms —1.00 mol of atoms. From left to right (top row): 65.4 g zinc, 12.0 g carbon, 24.3 g magnesium, and 63.5 g copper. From left to right (bottom row): 32.1 g sulfur, 28.1 g silicon, 207 g lead, and 118.7 g tin. (credit: modification of work by Mark Ott)

Because the definitions of both the mole and the atomic mass unit are based on the same reference substance, ^{12}C , the molar mass of any substance is numerically equivalent to its atomic or formula weight in amu. Per the amu definition, a single ^{12}C atom weighs 12 amu (its atomic mass is 12 amu). According to the definition of the mole, 12 g of ^{12}C contains 1 mole of ^{12}C atoms (its molar mass is 12 g/mol). This relationship holds for all elements, since their atomic masses are measured relative to that of the amu-reference substance, ^{12}C . Extending this principle, the molar mass of a compound in grams is likewise numerically equivalent to its formula mass in amu ([\[link\]](#)).

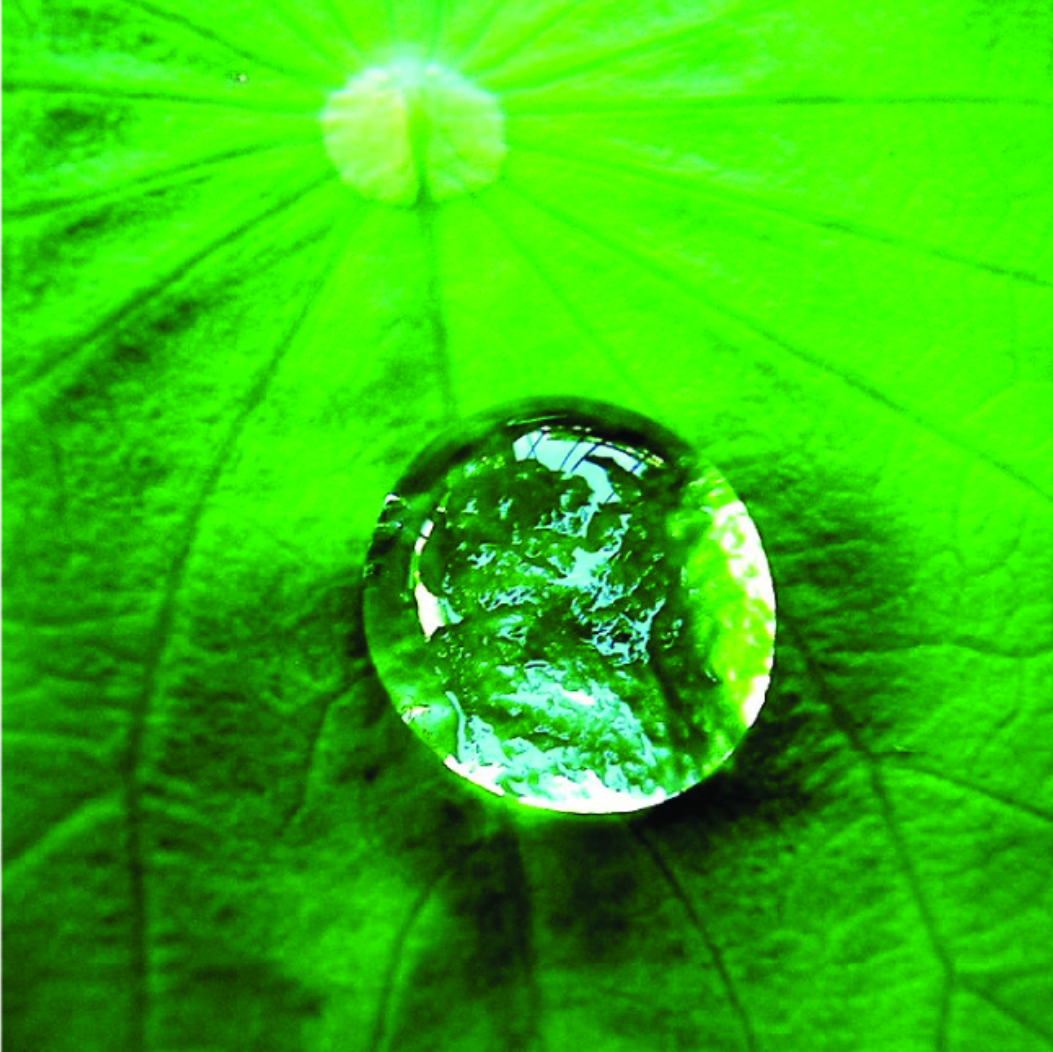


Each sample contains 6.02×10^{23} molecules or formula units—1.00 mol of the compound or element. Clock-wise from the upper left: 130.2 g of $\text{C}_8\text{H}_{17}\text{OH}$ (1-octanol, formula mass 130.2 amu), 454.4 g of HgI_2 (mercury(II) iodide, formula mass 454.4 amu), 32.0 g of CH_3OH (methanol, formula mass 32.0 amu) and 256.5 g of S_8 (sulfur, formula mass 256.5 amu). (credit: Sahar Atwa)

Element	Average Atomic Mass (amu)	Molar Mass (g/mol)	Atoms/Mole
C	12.01	12.01	6.022×10^{23}
H	1.008	1.008	6.022×10^{23}
O	16.00	16.00	6.022×10^{23}

Element	Average Atomic Mass (amu)	Molar Mass (g/mol)	Atoms/Mole
Na	22.99	22.99	6.022×10^{23}
Cl	35.45	35.45	6.022×10^{23}

While atomic mass and molar mass are numerically equivalent, keep in mind that they are vastly different in terms of scale, as represented by the vast difference in the magnitudes of their respective units (amu versus g). To appreciate the enormity of the mole, consider a small drop of water weighing about 0.03 g (see [\[link\]](#)). Although this represents just a tiny fraction of 1 mole of water (~18 g), it contains more water molecules than can be clearly imagined. If the molecules were distributed equally among the roughly seven billion people on earth, each person would receive more than 100 billion molecules.



The number of molecules in a single droplet of water is roughly 100 billion times greater than the number of people on earth. (credit: “tanakawho”/Wikimedia commons)

Note:



The mole is used in chemistry to represent 6.022×10^{23} of something, but it can be difficult to conceptualize such a large number. Watch this [video](#) and then complete the “Think” questions that follow. Explore more about the mole by reviewing the information under “Dig Deeper.”

The relationships between formula mass, the mole, and Avogadro’s number can be applied to compute various quantities that describe the composition of substances and compounds. For example, if we know the mass and chemical composition of a substance, we can determine the number of moles and calculate number of atoms or molecules in the sample. Likewise, if we know the number of moles of a substance, we can derive the number of atoms or molecules and calculate the substance’s mass.

Example:

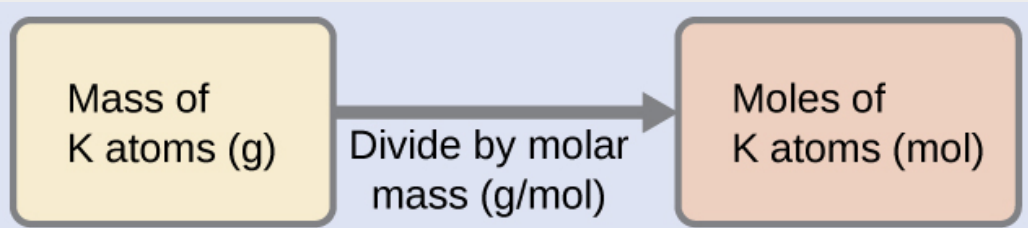
Deriving Moles from Grams for an Element

According to nutritional guidelines from the US Department of Agriculture, the estimated average requirement for dietary potassium is 4.7 g. What is the estimated average requirement of potassium in moles?

Solution

The mass of K is provided, and the corresponding amount of K in moles is requested. Referring to the periodic table, the atomic mass of K is 39.10 amu, and so its molar mass is 39.10 g/mol. The given mass of K (4.7 g) is a bit more than one-tenth the molar mass (39.10 g), so a reasonable “ballpark” estimate of the number of moles would be slightly greater than 0.1 mol.

The molar amount of a substance may be calculated by dividing its mass (g) by its molar mass (g/mol):



The factor-label method supports this mathematical approach since the unit “g” cancels and the answer has units of “mol.”

Equation:

$$4.7 \text{ g K} \left(\frac{\text{mol K}}{39.10 \text{ g}} \right) = 0.12 \text{ mol K}$$

The calculated magnitude (0.12 mol K) is consistent with our ballpark expectation, since it is a bit greater than 0.1 mol.

Check Your Learning

Beryllium is a light metal used to fabricate transparent X-ray windows for medical imaging instruments. How many moles of Be are in a thin-foil window weighing 3.24 g?

Note:

Answer:

0.360 mol

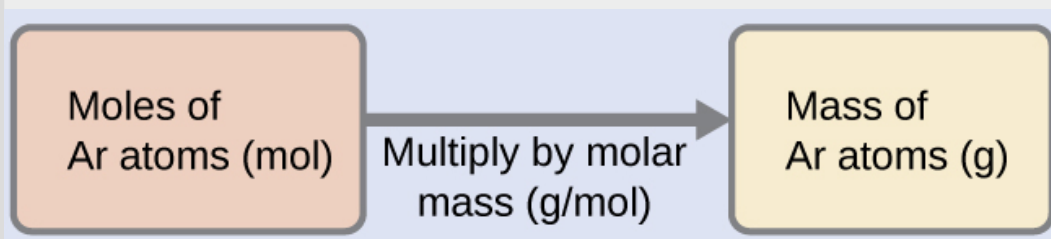
Example:

Deriving Grams from Moles for an Element

A liter of air contains 9.2×10^{-4} mol argon. What is the mass of Ar in a liter of air?

Solution

The molar amount of Ar is provided and must be used to derive the corresponding mass in grams. Since the amount of Ar is less than 1 mole, the mass will be less than the mass of 1 mole of Ar, approximately 40 g. The molar amount in question is approximately one-one thousandth ($\sim 10^{-3}$) of a mole, and so the corresponding mass should be roughly one-one thousandth of the molar mass (~ 0.04 g):



In this case, logic dictates (and the factor-label method supports) multiplying the provided amount (mol) by the molar mass (g/mol):

Equation:

$$9.2 \times 10^{-4} \text{ mol Ar} \left(\frac{39.95 \text{ g}}{\text{mol Ar}} \right) = 0.037 \text{ g Ar}$$

The result is in agreement with our expectations, around 0.04 g Ar.

Check Your Learning

What is the mass of 2.561 mol of gold?

Note:

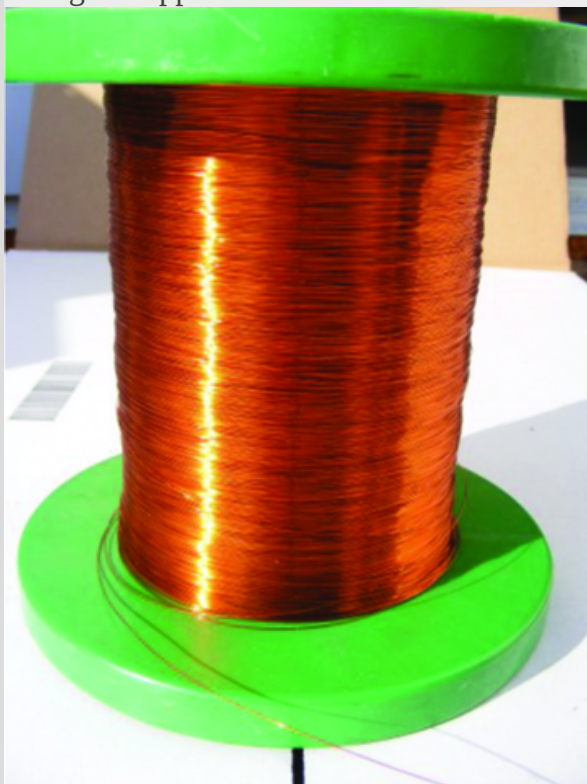
Answer:

504.4 g

Example:

Deriving Number of Atoms from Mass for an Element

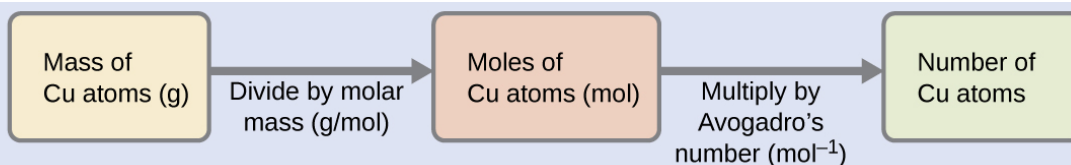
Copper is commonly used to fabricate electrical wire ([link](#)). How many copper atoms are in 5.00 g of copper wire?



Copper wire is composed of many, many atoms of Cu. (credit: Emilian Robert Vicol)

Solution

The number of Cu atoms in the wire may be conveniently derived from its mass by a two-step computation: first calculating the molar amount of Cu, and then using Avogadro's number (N_A) to convert this molar amount to number of Cu atoms:



Considering that the provided sample mass (5.00 g) is a little less than one-tenth the mass of 1 mole of Cu (~64 g), a reasonable estimate for the number of atoms in the sample would be on the order of one-tenth N_A , or approximately 10^{22} Cu atoms. Carrying out the two-step computation yields:

Equation:

$$5.00 \text{ g Cu} \left(\frac{\cancel{\text{mol Cu}}}{63.55 \cancel{\text{ g}}} \right) \left(\frac{6.022 \times 10^{23} \text{ atoms}}{\cancel{\text{mol}}} \right) = 4.74 \times 10^{22} \text{ atoms of copper}$$

The factor-label method yields the desired cancellation of units, and the computed result is on the order of 10^{22} as expected.

Check Your Learning

A prospector panning for gold in a river collects 15.00 g of pure gold. How many Au atoms are in this quantity of gold?

Note:

Answer:

4.586×10^{22} Au atoms

Example:

Deriving Moles from Grams for a Compound

Our bodies synthesize protein from amino acids. One of these amino acids is glycine, which has the molecular formula $\text{C}_2\text{H}_5\text{O}_2\text{N}$. How many moles of glycine molecules are contained in 28.35 g of glycine?

Solution

We can derive the number of moles of a compound from its mass following the same procedure we used for an element in [\[link\]](#):

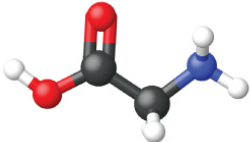
Mass of
 $\text{C}_2\text{H}_5\text{O}_2\text{N}$ (g)

Divide by molar
mass (g/mol)

Moles of
 $\text{C}_2\text{H}_5\text{O}_2\text{N}$ (mol)

The molar mass of glycine is required for this calculation, and it is computed in the same fashion as its molecular mass. One mole of glycine, $\text{C}_2\text{H}_5\text{O}_2\text{N}$, contains 2 moles of carbon, 5 moles of hydrogen, 2 moles of oxygen, and 1 mole of nitrogen:

Element	Quantity (mol element/ mol compound)		Molar mass (g/mol element)		Subtotal (g/mol compound)
C	2	×	12.01	=	24.02
H	5	×	1.008	=	5.040
O	2	×	16.00	=	32.00
N	1	×	14.007	=	14.007
Molecular mass (g/mol compound)					75.07



The provided mass of glycine (~28 g) is a bit more than one-third the molar mass (~75 g/mol), so we would expect the computed result to be a bit greater than one-third of a mole (~0.33 mol). Dividing the compound's mass by its molar mass yields:

Equation:

$$28.35 \text{ g glycine} \left(\frac{\text{mol glycine}}{75.07 \text{ g}} \right) = 0.378 \text{ mol glycine}$$

This result is consistent with our rough estimate.

Check Your Learning

How many moles of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, are in a 25-g sample of sucrose?

Note:

Answer:

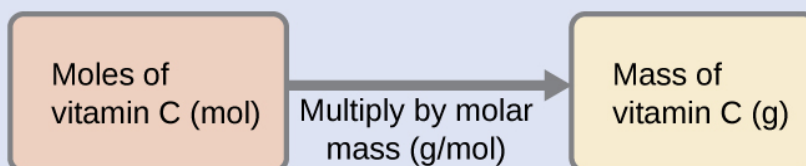
0.073 mol

Example:**Deriving Grams from Moles for a Compound**

Vitamin C is a covalent compound with the molecular formula $\text{C}_6\text{H}_8\text{O}_6$. The recommended daily dietary allowance of vitamin C for children aged 4–8 years is 1.42×10^{-4} mol. What is the mass of this allowance in grams?

Solution

As for elements, the mass of a compound can be derived from its molar amount as shown:



The molar mass for this compound is computed to be 176.124 g/mol. The given number of moles is a very small fraction of a mole ($\sim 10^{-4}$ or one-ten thousandth); therefore, we would expect the corresponding mass to be about one-ten thousandth of the molar mass (~ 0.02 g). Performing the calculation, we get:

Equation:

$$1.42 \times 10^{-4} \text{ mol vitamin C} \left(\frac{176.124 \text{ g}}{\text{mol vitamin C}} \right) = 0.0250 \text{ g vitamin C}$$

This is consistent with the anticipated result.

Check Your Learning

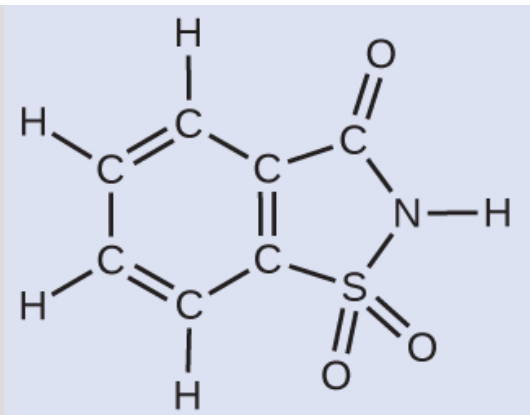
What is the mass of 0.443 mol of hydrazine, N_2H_4 ?

Note:**Answer:**

14.2 g

Example:**Deriving the Number of Atoms and Molecules from the Mass of a Compound**

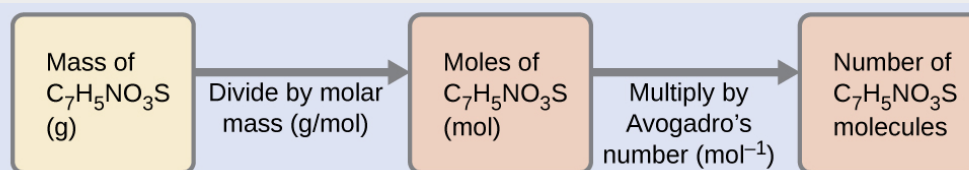
A packet of an artificial sweetener contains 40.0 mg of saccharin ($\text{C}_7\text{H}_5\text{NO}_3\text{S}$), which has the structural formula:



Given that saccharin has a molar mass of 183.18 g/mol, how many saccharin molecules are in a 40.0-mg (0.0400-g) sample of saccharin? How many carbon atoms are in the same sample?

Solution

The number of molecules in a given mass of compound is computed by first deriving the number of moles, as demonstrated in [\[link\]](#), and then multiplying by Avogadro's number:



Using the provided mass and molar mass for saccharin yields:

Equation:

$$0.0400 \text{ g C}_7\text{H}_5\text{NO}_3\text{S} \left(\frac{1 \text{ mol C}_7\text{H}_5\text{NO}_3\text{S}}{183.18 \text{ g C}_7\text{H}_5\text{NO}_3\text{S}} \right) \left(\frac{6.022 \times 10^{23} \text{ C}_7\text{H}_5\text{NO}_3\text{S molecules}}{1 \text{ mol C}_7\text{H}_5\text{NO}_3\text{S}} \right) = 1.31 \times 10^{20} \text{ C}_7\text{H}_5\text{NO}_3\text{S molecules}$$

The compound's formula shows that each molecule contains seven carbon atoms, and so the number of C atoms in the provided sample is:

Equation:

$$1.31 \times 10^{20} \text{ C}_7\text{H}_5\text{NO}_3\text{S molecules} \left(\frac{7 \text{ C atoms}}{1 \text{ C}_7\text{H}_5\text{NO}_3\text{S molecule}} \right) = 9.17 \times 10^{20} \text{ C atoms}$$

Check Your Learning

How many C_4H_{10} molecules are contained in 9.213 g of this compound? How many hydrogen atoms?

Note:

Answer:

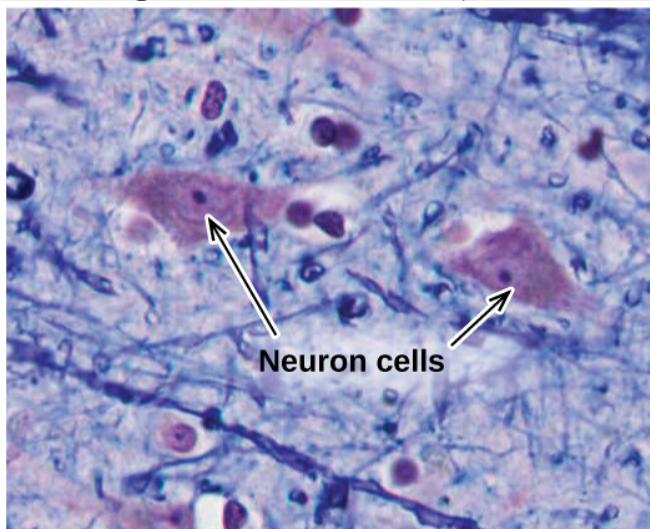
9.545×10^{22} molecules C_4H_{10} ; 9.545×10^{23} atoms H

Note:**Counting Neurotransmitter Molecules in the Brain**

The brain is the control center of the central nervous system ([\[link\]](#)). It sends and receives signals to and from muscles and other internal organs to monitor and control their functions; it processes stimuli detected by sensory organs to guide interactions with the external world; and it houses the complex physiological processes that give rise to our intellect and emotions. The broad field of neuroscience spans all aspects of the structure and function of the central nervous system, including research on the anatomy and physiology of the brain. Great progress has been made in brain research over the past few decades, and the BRAIN Initiative, a federal initiative announced in 2013, aims to accelerate and capitalize on these advances through the concerted efforts of various industrial, academic, and government agencies (more details available at www.whitehouse.gov/share/brain-initiative).



(a)

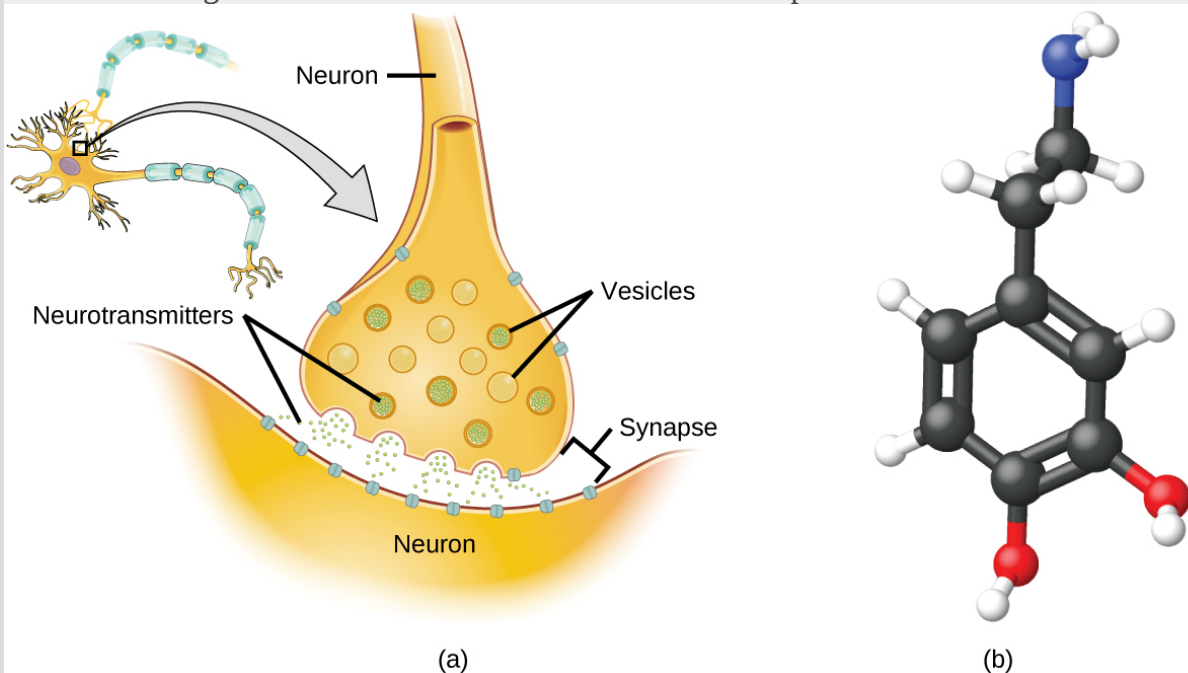


(b)

- (a) A typical human brain weighs about 1.5 kg and occupies a volume of roughly 1.1 L.
(b) Information is transmitted in brain tissue and throughout the central nervous system by specialized cells called neurons (micrograph shows cells at 1600 \times magnification).

Specialized cells called neurons transmit information between different parts of the central nervous system by way of electrical and chemical signals. Chemical signaling occurs at the interface between different neurons when one of the cells releases molecules (called neurotransmitters) that diffuse across the small gap between the cells (called the synapse)

and bind to the surface of the other cell. These neurotransmitter molecules are stored in small intracellular structures called vesicles that fuse to the cell wall and then break open to release their contents when the neuron is appropriately stimulated. This process is called exocytosis (see [link](#)). One neurotransmitter that has been very extensively studied is dopamine, $C_8H_{11}NO_2$. Dopamine is involved in various neurological processes that impact a wide variety of human behaviors. Dysfunctions in the dopamine systems of the brain underlie serious neurological diseases such as Parkinson's and schizophrenia.



(a) Chemical signals are transmitted from neurons to other cells by the release of neurotransmitter molecules into the small gaps (synapses) between the cells. (b) Dopamine, $C_8H_{11}NO_2$, is a neurotransmitter involved in a number of neurological processes.

One important aspect of the complex processes related to dopamine signaling is the number of neurotransmitter molecules released during exocytosis. Since this number is a central factor in determining neurological response (and subsequent human thought and action), it is important to know how this number changes with certain controlled stimulations, such as the administration of drugs. It is also important to understand the mechanism responsible for any changes in the number of neurotransmitter molecules released—for example, some dysfunction in exocytosis, a change in the number of vesicles in the neuron, or a change in the number of neurotransmitter molecules in each vesicle.

Significant progress has been made recently in directly measuring the number of dopamine molecules stored in individual vesicles and the amount actually released when the vesicle undergoes exocytosis. Using miniaturized probes that can selectively detect dopamine molecules in very small amounts, scientists have determined that the vesicles of a certain type of mouse brain neuron contain an average of 30,000 dopamine molecules per vesicle

(about 5×10^{-20} mol or 50 zmol). Analysis of these neurons from mice subjected to various drug therapies shows significant changes in the average number of dopamine molecules contained in individual vesicles, increasing or decreasing by up to three-fold, depending on the specific drug used. These studies also indicate that not all of the dopamine in a given vesicle is released during exocytosis, suggesting that it may be possible to regulate the fraction released using pharmaceutical therapies.[\[footnote\]](#)

Omiatek, Donna M., Amanda J. Bressler, Ann-Sofie Cans, Anne M. Andrews, Michael L. Heien, and Andrew G. Ewing. "The Real Catecholamine Content of Secretory Vesicles in the CNS Revealed by Electrochemical Cytometry." *Scientific Report* 3 (2013): 1447, accessed January 14, 2015, doi:10.1038/srep01447.

Key Concepts and Summary

The formula mass of a substance is the sum of the average atomic masses of each atom represented in the chemical formula and is expressed in atomic mass units. The formula mass of a covalent compound is also called the molecular mass. A convenient amount unit for expressing very large numbers of atoms or molecules is the mole. Experimental measurements have determined the number of entities composing 1 mole of substance to be 6.022×10^{23} , a quantity called Avogadro's number. The mass in grams of 1 mole of substance is its molar mass. Due to the use of the same reference substance in defining the atomic mass unit and the mole, the formula mass (amu) and molar mass (g/mol) for any substance are numerically equivalent (for example, one H_2O molecule weighs approximately 18 amu and 1 mole of H_2O molecules weighs approximately 18 g).

Chemistry End of Chapter Exercises

Exercise:

Problem: What is the total mass (amu) of carbon in each of the following molecules?

- (a) CH_4
- (b) CHCl_3
- (c) $\text{C}_{12}\text{H}_{10}\text{O}_6$
- (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

Solution:

(a) 12.01 amu; (b) 12.01 amu; (c) 144.12 amu; (d) 60.05 amu

Exercise:

Problem: What is the total mass of hydrogen in each of the molecules?

- (a) CH_4
- (b) CHCl_3
- (c) $\text{C}_{12}\text{H}_{10}\text{O}_6$
- (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

Exercise:

Problem: Calculate the molecular or formula mass of each of the following:

- (a) P_4
 - (b) H_2O
 - (c) $\text{Ca}(\text{NO}_3)_2$
 - (d) $\text{CH}_3\text{CO}_2\text{H}$ (acetic acid)
 - (e) $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (sucrose, cane sugar).
-

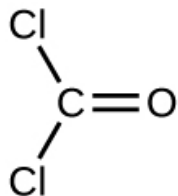
Solution:

(a) 123.896 amu; (b) 18.015 amu; (c) 164.086 amu; (d) 60.052 amu; (e) 342.297 amu

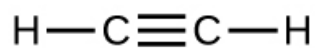
Exercise:

Problem: Determine the molecular mass of the following compounds:

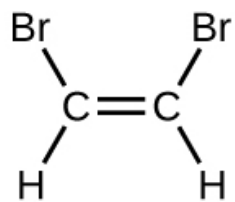
(a)



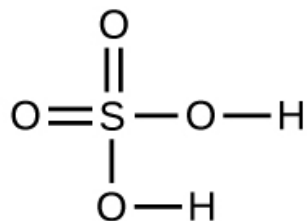
(b)



(c)



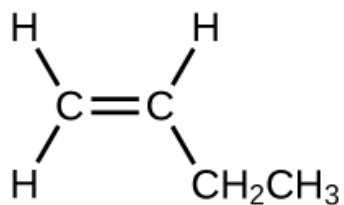
(d)



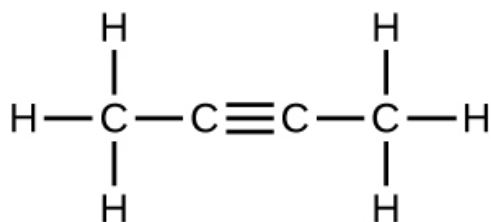
Exercise:

Problem: Determine the molecular mass of the following compounds:

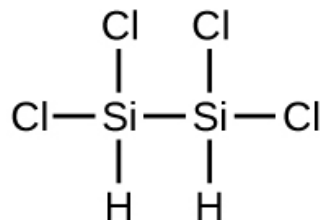
(a)



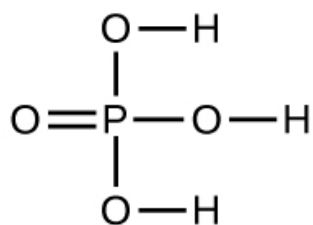
(b)



(c)



(d)



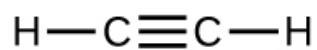
Solution:

- (a) 56.107 amu;
- (b) 54.091 amu;
- (c) 199.9976 amu;
- (d) 97.9950 amu

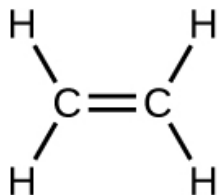
Exercise:

Problem: Which molecule has a molecular mass of 28.05 amu?

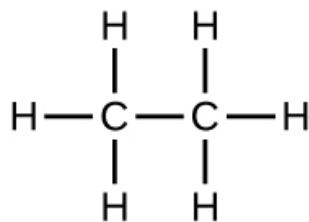
(a)



(b)



(c)



Exercise:

Problem:

Write a sentence that describes how to determine the number of moles of a compound in a known mass of the compound if we know its molecular formula.

Solution:

Use the molecular formula to find the molar mass; to obtain the number of moles, divide the mass of compound by the molar mass of the compound expressed in grams.

Exercise:

Problem: Compare 1 mole of H_2 , 1 mole of O_2 , and 1 mole of F_2 .

(a) Which has the largest number of molecules? Explain why.

(b) Which has the greatest mass? Explain why.

Exercise:**Problem:**

Which contains the greatest mass of oxygen: 0.75 mol of ethanol ($\text{C}_2\text{H}_5\text{OH}$), 0.60 mol of formic acid (HCO_2H), or 1.0 mol of water (H_2O)? Explain why.

Solution:

Formic acid. Its formula has twice as many oxygen atoms as the other two compounds (one each). Therefore, 0.60 mol of formic acid would be equivalent to 1.20 mol of a compound containing a single oxygen atom.

Exercise:**Problem:**

Which contains the greatest number of moles of oxygen atoms: 1 mol of ethanol ($\text{C}_2\text{H}_5\text{OH}$), 1 mol of formic acid (HCO_2H), or 1 mol of water (H_2O)? Explain why.

Exercise:**Problem:**

How are the molecular mass and the molar mass of a compound similar and how are they different?

Solution:

The two masses have the same numerical value, but the units are different: The molecular mass is the mass of 1 molecule while the molar mass is the mass of 6.022×10^{23} molecules.

Exercise:

Problem: Calculate the molar mass of each of the following compounds:

- (a) hydrogen fluoride, HF
- (b) ammonia, NH_3
- (c) nitric acid, HNO_3
- (d) silver sulfate, Ag_2SO_4
- (e) boric acid, $\text{B}(\text{OH})_3$

Exercise:

Problem: Calculate the molar mass of each of the following:

- (a) S_8
 - (b) C_5H_{12}
 - (c) $\text{Sc}_2(\text{SO}_4)_3$
 - (d) CH_3COCH_3 (acetone)
 - (e) $\text{C}_6\text{H}_{12}\text{O}_6$ (glucose)
-

Solution:

(a) 256.528 g/mol; (b) 72.150 g mol⁻¹; (c) 378.103 g mol⁻¹; (d) 58.080 g mol⁻¹; (e) 180.158 g mol⁻¹

Exercise:

Problem:

Calculate the empirical or molecular formula mass and the molar mass of each of the following minerals:

- (a) limestone, CaCO_3
- (b) halite, NaCl
- (c) beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$
- (d) malachite, $\text{Cu}_2(\text{OH})_2\text{CO}_3$
- (e) turquoise, $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8(\text{H}_2\text{O})_4$

Exercise:

Problem: Calculate the molar mass of each of the following:

(a) the anesthetic halothane, $\text{C}_2\text{HBrClF}_3$

(b) the herbicide paraquat, $\text{C}_{12}\text{H}_{14}\text{N}_2\text{Cl}_2$

(c) caffeine, $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$

(d) urea, $\text{CO}(\text{NH}_2)_2$

(e) a typical soap, $\text{C}_{17}\text{H}_{35}\text{CO}_2\text{Na}$

Solution:

(a) $197.382 \text{ g mol}^{-1}$; (b) $257.163 \text{ g mol}^{-1}$; (c) $194.193 \text{ g mol}^{-1}$; (d) $60.056 \text{ g mol}^{-1}$; (e) $306.464 \text{ g mol}^{-1}$

Exercise:

Problem:

Determine the number of moles of compound and the number of moles of each type of atom in each of the following:

(a) 25.0 g of propylene, C_3H_6

(b) $3.06 \times 10^{-3} \text{ g}$ of the amino acid glycine, $\text{C}_2\text{H}_5\text{NO}_2$

(c) 25 lb of the herbicide Treflan, $\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_4\text{F}$ (1 lb = 454 g)

(d) 0.125 kg of the insecticide Paris Green, $\text{Cu}_4(\text{AsO}_3)_2(\text{CH}_3\text{CO}_2)_2$

(e) 325 mg of aspirin, $\text{C}_6\text{H}_4(\text{CO}_2\text{H})(\text{CO}_2\text{CH}_3)$

Exercise:

Problem: Determine the mass of each of the following:

(a) 0.0146 mol KOH

(b) 10.2 mol ethane, C_2H_6

(c) $1.6 \times 10^{-3} \text{ mol}$ Na_2SO_4

(d) $6.854 \times 10^3 \text{ mol}$ glucose, $\text{C}_6\text{H}_{12}\text{O}_6$

(e) 2.86 mol $\text{Co}(\text{NH}_3)_6\text{Cl}_3$

Solution:

- (a) 0.819 g;
- (b) 307 g;
- (c) 0.23 g;
- (d) 1.235×10^6 g (1235 kg);
- (e) 765 g

Exercise:

Problem:

Determine the number of moles of the compound and determine the number of moles of each type of atom in each of the following:

- (a) 2.12 g of potassium bromide, KBr
- (b) 0.1488 g of phosphoric acid, H_3PO_4
- (c) 23 kg of calcium carbonate, CaCO_3
- (d) 78.452 g of aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$
- (e) 0.1250 mg of caffeine, $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$

Exercise:

Problem: Determine the mass of each of the following:

- (a) 2.345 mol LiCl
- (b) 0.0872 mol acetylene, C_2H_2
- (c) 3.3×10^{-2} mol Na_2CO_3
- (d) 1.23×10^3 mol fructose, $\text{C}_6\text{H}_{12}\text{O}_6$
- (e) 0.5758 mol $\text{FeSO}_4(\text{H}_2\text{O})_7$

Solution:

- (a) 99.41 g;
- (b) 2.27 g;
- (c) 3.5 g;
- (d) 222 kg;
- (e) 160.1 g

Exercise:

Problem:

The approximate minimum daily dietary requirement of the amino acid leucine, $\text{C}_6\text{H}_{13}\text{NO}_2$, is 1.1 g. What is this requirement in moles?

Exercise:

Problem: Determine the mass in grams of each of the following:

- (a) 0.600 mol of oxygen atoms
- (b) 0.600 mol of oxygen molecules, O_2
- (c) 0.600 mol of ozone molecules, O_3

Solution:

(a) 9.60 g; (b) 19.2 g; (c) 28.8 g

Exercise:**Problem:**

A 55-kg woman has 7.5×10^{-3} mol of hemoglobin (molar mass = 64,456 g/mol) in her blood. How many hemoglobin molecules is this? What is this quantity in grams?

Exercise:**Problem:**

Determine the number of atoms and the mass of zirconium, silicon, and oxygen found in 0.3384 mol of zircon, ZrSiO_4 , a semiprecious stone.

Solution:

zirconium: 2.038×10^{23} atoms; 30.87 g; silicon: 2.038×10^{23} atoms; 9.504 g; oxygen: 8.151×10^{23} atoms; 21.66 g

Exercise:**Problem:**

Determine which of the following contains the greatest mass of hydrogen: 1 mol of CH_4 , 0.6 mol of C_6H_6 , or 0.4 mol of C_3H_8 .

Exercise:**Problem:**

Determine which of the following contains the greatest mass of aluminum: 122 g of AlPO_4 , 266 g of Al_2Cl_6 , or 225 g of Al_2S_3 .

Solution:

AlPO_4 : 1.000 mol, or 26.98 g Al

Al_2Cl_6 : 1.994 mol, or 53.74 g Al

Al_2S_3 : 3.00 mol, or 80.94 g Al

The Al_2S_3 sample thus contains the greatest mass of Al.

Exercise:**Problem:**

Diamond is one form of elemental carbon. An engagement ring contains a diamond weighing 1.25 carats (1 carat = 200 mg). How many atoms are present in the diamond?

Exercise:**Problem:**

The Cullinan diamond was the largest natural diamond ever found (January 25, 1905). It weighed 3104 carats (1 carat = 200 mg). How many carbon atoms were present in the stone?

Solution:

3.113×10^{25} C atoms

Exercise:**Problem:**

One 55-gram serving of a particular cereal supplies 270 mg of sodium, 11% of the recommended daily allowance. How many moles and atoms of sodium are in the recommended daily allowance?

Exercise:**Problem:**

A certain nut crunch cereal contains 11.0 grams of sugar (sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$) per serving size of 60.0 grams. How many servings of this cereal must be eaten to consume 0.0278 moles of sugar?

Solution:

0.865 servings, or about 1 serving.

Exercise:**Problem:**

A tube of toothpaste contains 0.76 g of sodium monofluorophosphate ($\text{Na}_2\text{PO}_3\text{F}$) in 100 mL.

(a) What mass of fluorine atoms in mg was present?

(b) How many fluorine atoms were present?

Exercise:

Problem: Which of the following represents the least number of molecules?

(a) 20.0 g of H_2O (18.02 g/mol)

(b) 77.0 g of CH_4 (16.06 g/mol)

(c) 68.0 g of CaH_2 (42.09 g/mol)

(d) 100.0 g of N_2O (44.02 g/mol)

(e) 84.0 g of HF (20.01 g/mol)

Solution:

20.0 g H_2O represents the least number of molecules since it has the least number of moles.

Glossary

Avogadro's number (N_A)

experimentally determined value of the number of entities comprising 1 mole of substance, equal to $6.022 \times 10^{23} \text{ mol}^{-1}$

formula mass

sum of the average masses for all atoms represented in a chemical formula; for covalent compounds, this is also the molecular mass

molar mass

mass in grams of 1 mole of a substance

mole

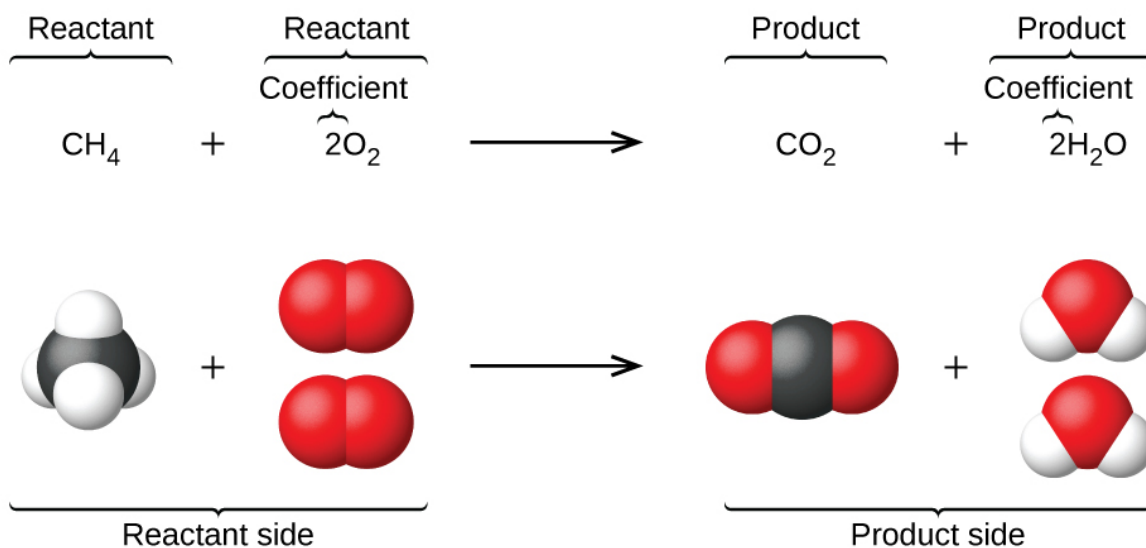
amount of substance containing the same number of atoms, molecules, ions, or other entities as the number of atoms in exactly 12 grams of ^{12}C

Writing and Balancing Chemical Equations

By the end of this section, you will be able to:

- Derive chemical equations from narrative descriptions of chemical reactions.
- Write and balance chemical equations in molecular, total ionic, and net ionic formats.

The preceding chapter introduced the use of element symbols to represent individual atoms. When atoms gain or lose electrons to yield ions, or combine with other atoms to form molecules, their symbols are modified or combined to generate chemical formulas that appropriately represent these species. Extending this symbolism to represent both the identities and the relative quantities of substances undergoing a chemical (or physical) change involves writing and balancing a **chemical equation**. Consider as an example the reaction between one methane molecule (CH_4) and two diatomic oxygen molecules (O_2) to produce one carbon dioxide molecule (CO_2) and two water molecules (H_2O). The chemical equation representing this process is provided in the upper half of [\[link\]](#), with space-filling molecular models shown in the lower half of the figure.



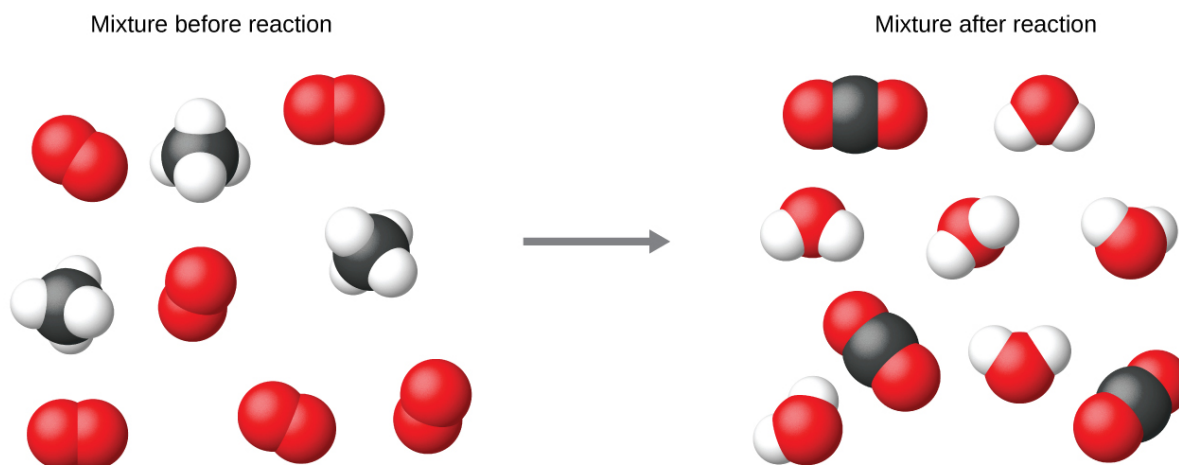
The reaction between methane and oxygen to yield carbon dioxide and water (shown at bottom) may be represented by a chemical equation using formulas (top).

This example illustrates the fundamental aspects of any chemical equation:

1. The substances undergoing reaction are called **reactants**, and their formulas are placed on the left side of the equation.
2. The substances generated by the reaction are called **products**, and their formulas are placed on the right side of the equation.
3. Plus signs (+) separate individual reactant and product formulas, and an arrow (\longrightarrow) separates the reactant and product (left and right) sides of the equation.
4. The relative numbers of reactant and product species are represented by **coefficients** (numbers placed immediately to the left of each formula). A coefficient of 1 is typically omitted.

It is common practice to use the smallest possible whole-number coefficients in a chemical equation, as is done in this example. Realize, however, that these coefficients represent the *relative* numbers of reactants and products, and, therefore, they may be correctly interpreted as ratios. Methane and oxygen react to yield carbon dioxide and water in a 1:2:1:2 ratio. This ratio is satisfied if the numbers of these molecules are, respectively, 1-2-1-2, or 2-4-2-4, or 3-6-3-6, and so on ([\[link\]](#)). Likewise, these coefficients may be interpreted with regard to any amount (number) unit, and so this equation may be correctly read in many ways, including:

- One methane molecule and two oxygen molecules react to yield one carbon dioxide molecule and two water molecules.
- One dozen methane molecules and two dozen oxygen molecules react to yield one dozen carbon dioxide molecules and two dozen water molecules.
- One mole of methane molecules and 2 moles of oxygen molecules react to yield 1 mole of carbon dioxide molecules and 2 moles of water molecules.



Regardless of the absolute numbers of molecules involved, the ratios between numbers of molecules of each species that react (the reactants) and molecules of each species that form (the products) are the same and are given by the chemical reaction equation.

Balancing Equations

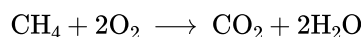
The chemical equation described in section 4.1 is **balanced**, meaning that equal numbers of atoms for each element involved in the reaction are represented on the reactant and product sides. This is a requirement the equation must satisfy to be consistent with the law of conservation of matter. It may be confirmed by simply summing the numbers of atoms on either side of the arrow and comparing these sums to ensure they are equal. Note that the number of atoms for a given element is calculated by multiplying the coefficient of any formula containing that element by the element's subscript in the formula. If an element appears in more than one formula on a given side of the equation, the number of atoms represented in each must be computed and then added together. For example, both product species in the example reaction, CO_2 and H_2O , contain the element oxygen, and so the number of oxygen atoms on the product side of the equation is

Equation:

$$\left(1 \text{ CO}_2 \text{ molecule} \times \frac{2 \text{ O atoms}}{\text{CO}_2 \text{ molecule}} \right) + \left(2 \text{ H}_2\text{O molecules} \times \frac{1 \text{ O atom}}{\text{H}_2\text{O molecule}} \right) = 4 \text{ O atoms}$$

The equation for the reaction between methane and oxygen to yield carbon dioxide and water is confirmed to be balanced per this approach, as shown here:

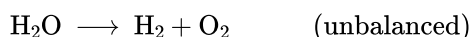
Equation:



Element	Reactants	Products	Balanced?
C	$1 \times 1 = 1$	$1 \times 1 = 1$	$1 = 1$, yes
H	$4 \times 1 = 4$	$2 \times 2 = 4$	$4 = 4$, yes
O	$2 \times 2 = 4$	$(1 \times 2) + (2 \times 1) = 4$	$4 = 4$, yes

A balanced chemical equation often may be derived from a qualitative description of some chemical reaction by a fairly simple approach known as balancing by inspection. Consider as an example the decomposition of water to yield molecular hydrogen and oxygen. This process is represented qualitatively by an *unbalanced* chemical equation:

Equation:

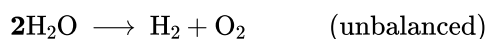


Comparing the number of H and O atoms on either side of this equation confirms its imbalance:

Element	Reactants	Products	Balanced?
H	$1 \times 2 = 2$	$1 \times 2 = 2$	$2 = 2$, yes
O	$1 \times 1 = 1$	$1 \times 2 = 2$	$1 \neq 2$, no

The numbers of H atoms on the reactant and product sides of the equation are equal, but the numbers of O atoms are not. To achieve balance, the *coefficients* of the equation may be changed as needed. Keep in mind, of course, that the *formula subscripts* define, in part, the identity of the substance, and so these cannot be changed without altering the qualitative meaning of the equation. For example, changing the reactant formula from H_2O to H_2O_2 would yield balance in the number of atoms, but doing so also changes the reactant's identity (it's now hydrogen peroxide and not water). The O atom balance may be achieved by changing the coefficient for H_2O to 2.

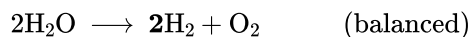
Equation:



Element	Reactants	Products	Balanced?
H	$2 \times 2 = 4$	$1 \times 2 = 2$	$4 \neq 2$, no
O	$2 \times 1 = 2$	$1 \times 2 = 2$	$2 = 2$, yes

The H atom balance was upset by this change, but it is easily reestablished by changing the coefficient for the H_2 product to 2.

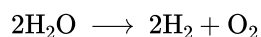
Equation:



Element	Reactants	Products	Balanced?
H	$2 \times 2 = 4$	$2 \times 2 = 4$	$4 = 4$, yes
O	$2 \times 1 = 2$	$1 \times 2 = 2$	$2 = 2$, yes

These coefficients yield equal numbers of both H and O atoms on the reactant and product sides, and the balanced equation is, therefore:

Equation:



Example:

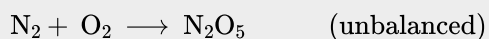
Balancing Chemical Equations

Write a balanced equation for the reaction of molecular nitrogen (N_2) and oxygen (O_2) to form dinitrogen pentoxide.

Solution

First, write the unbalanced equation.

Equation:



Next, count the number of each type of atom present in the unbalanced equation.

Element	Reactants	Products	Balanced?
N	$1 \times 2 = 2$	$1 \times 2 = 2$	$2 = 2$, yes
O	$1 \times 2 = 2$	$1 \times 5 = 5$	$2 \neq 5$, no

Though nitrogen is balanced, changes in coefficients are needed to balance the number of oxygen atoms. To balance the number of oxygen atoms, a reasonable first attempt would be to change the coefficients for the O_2 and N_2O_5 to integers that will yield 10 O atoms (the least common multiple for the O atom subscripts in these two formulas).

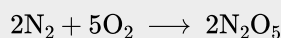
Equation:



Element	Reactants	Products	Balanced?
N	$1 \times 2 = 2$	$2 \times 2 = 4$	$2 \neq 4$, no
O	$5 \times 2 = 10$	$2 \times 5 = 10$	$10 = 10$, yes

The N atom balance has been upset by this change; it is restored by changing the coefficient for the reactant N₂ to 2.

Equation:



Element	Reactants	Products	Balanced?
N	$2 \times 2 = 4$	$2 \times 2 = 4$	$4 = 4$, yes
O	$5 \times 2 = 10$	$2 \times 5 = 10$	$10 = 10$, yes

The numbers of N and O atoms on either side of the equation are now equal, and so the equation is balanced.

Check Your Learning

Write a balanced equation for the decomposition of ammonium nitrate to form molecular nitrogen, molecular oxygen, and water. (Hint: Balance oxygen last, since it is present in more than one molecule on the right side of the equation.)

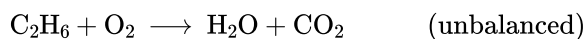
Note:

Answer:



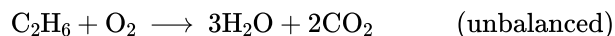
It is sometimes convenient to use fractions instead of integers as intermediate coefficients in the process of balancing a chemical equation. When balance is achieved, all the equation's coefficients may then be multiplied by a whole number to convert the fractional coefficients to integers without upsetting the atom balance. For example, consider the reaction of ethane (C₂H₆) with oxygen to yield H₂O and CO₂, represented by the unbalanced equation:

Equation:



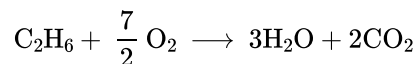
Following the usual inspection approach, one might first balance C and H atoms by changing the coefficients for the two product species, as shown:

Equation:



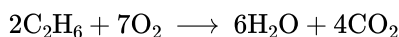
This results in seven O atoms on the product side of the equation, an odd number—no integer coefficient can be used with the O_2 reactant to yield an odd number, so a fractional coefficient, $\frac{7}{2}$, is used instead to yield a provisional balanced equation:

Equation:



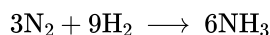
A conventional balanced equation with integer-only coefficients is derived by multiplying each coefficient by 2:

Equation:



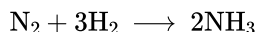
Finally with regard to balanced equations, recall that convention dictates use of the *smallest whole-number coefficients*. Although the equation for the reaction between molecular nitrogen and molecular hydrogen to produce ammonia is, indeed, balanced,

Equation:



the coefficients are not the smallest possible integers representing the relative numbers of reactant and product molecules. Dividing each coefficient by the greatest common factor, 3, gives the preferred equation:

Equation:



Note:

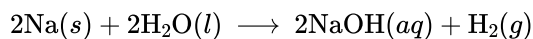


Use this interactive [tutorial](#) for additional practice balancing equations.

Additional Information in Chemical Equations

The physical states of reactants and products in chemical equations very often are indicated with a parenthetical abbreviation following the formulas. Common abbreviations include *s* for solids, *l* for liquids, *g* for gases, and *aq* for substances dissolved in water (*aqueous solutions*, as introduced in the preceding chapter). These notations are illustrated in the example equation here:

Equation:

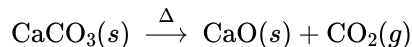


This equation represents the reaction that takes place when sodium metal is placed in water. The solid sodium reacts with liquid water to produce molecular hydrogen gas and the ionic compound sodium hydroxide (a solid in

pure form, but readily dissolved in water).

Special conditions necessary for a reaction are sometimes designated by writing a word or symbol above or below the equation's arrow. For example, a reaction carried out by heating may be indicated by the uppercase Greek letter delta (Δ) over the arrow.

Equation:

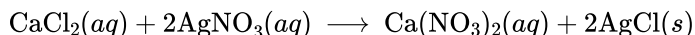


Other examples of these special conditions will be encountered in more depth in later chapters.

Equations for Ionic Reactions

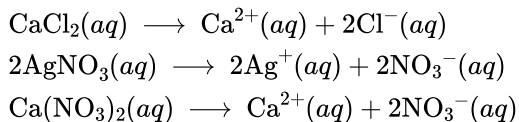
Given the abundance of water on earth, it stands to reason that a great many chemical reactions take place in aqueous media. When ions are involved in these reactions, the chemical equations may be written with various levels of detail appropriate to their intended use. To illustrate this, consider a reaction between ionic compounds taking place in an aqueous solution. When aqueous solutions of CaCl_2 and AgNO_3 are mixed, a reaction takes place producing aqueous $\text{Ca}(\text{NO}_3)_2$ and solid AgCl :

Equation:



This balanced equation, derived in the usual fashion, is called a **molecular equation** because it doesn't explicitly represent the ionic species that are present in solution. When ionic compounds dissolve in water, they may *dissociate* into their constituent ions, which are subsequently dispersed homogeneously throughout the resulting solution (a thorough discussion of this important process is provided in the chapter on solutions). Ionic compounds dissolved in water are, therefore, more realistically represented as dissociated ions, in this case:

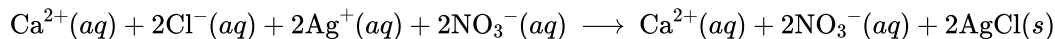
Equation:



Unlike these three ionic compounds, AgCl does not dissolve in water to a significant extent, as signified by its physical state notation, s .

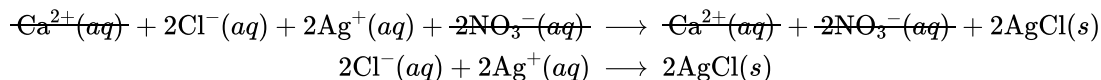
Explicitly representing all dissolved ions results in a **complete ionic equation**. In this particular case, the formulas for the dissolved ionic compounds are replaced by formulas for their dissociated ions:

Equation:



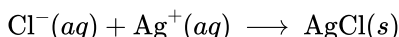
Examining this equation shows that two chemical species are present in identical form on both sides of the arrow, $\text{Ca}^{2+}(aq)$ and $\text{NO}_3^{-}(aq)$. These **spectator ions**—ions whose presence is required to maintain charge neutrality—are neither chemically nor physically changed by the process, and so they may be eliminated from the equation to yield a more succinct representation called a **net ionic equation**:

Equation:



Following the convention of using the smallest possible integers as coefficients, this equation is then written:

Equation:



This net ionic equation indicates that solid silver chloride may be produced from dissolved chloride and silver(I) ions, regardless of the source of these ions. These molecular and complete ionic equations provide additional information, namely, the ionic compounds used as sources of Cl^{-} and Ag^{+} .

Example:

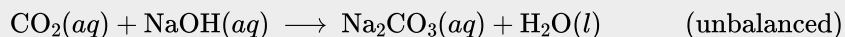
Molecular and Ionic Equations

When carbon dioxide is dissolved in an aqueous solution of sodium hydroxide, the mixture reacts to yield aqueous sodium carbonate and liquid water. Write balanced molecular, complete ionic, and net ionic equations for this process.

Solution

Begin by identifying formulas for the reactants and products and arranging them properly in chemical equation form:

Equation:



Balance is achieved easily in this case by changing the coefficient for NaOH to 2, resulting in the molecular equation for this reaction:

Equation:



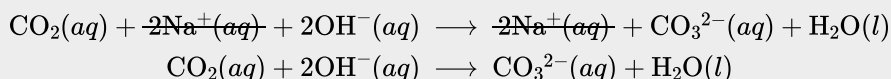
The two dissolved ionic compounds, NaOH and Na_2CO_3 , can be represented as dissociated ions to yield the complete ionic equation:

Equation:



Finally, identify the spectator ion(s), in this case $\text{Na}^{+}(aq)$, and remove it from each side of the equation to generate the net ionic equation:

Equation:



Check Your Learning

Diatomic chlorine and sodium hydroxide (lye) are commodity chemicals produced in large quantities, along with diatomic hydrogen, via the electrolysis of brine, according to the following unbalanced equation:

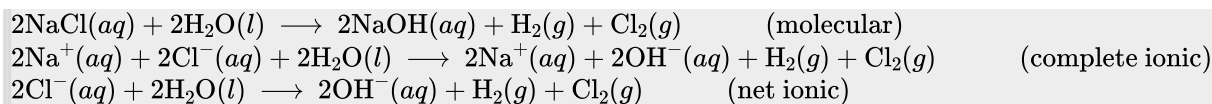
Equation:



Write balanced molecular, complete ionic, and net ionic equations for this process.

Note:

Answer:



Key Concepts and Summary

Chemical equations are symbolic representations of chemical and physical changes. Formulas for the substances undergoing the change (reactants) and substances generated by the change (products) are separated by an arrow and preceded by integer coefficients indicating their relative numbers. Balanced equations are those whose coefficients result in equal numbers of atoms for each element in the reactants and products. Chemical reactions in aqueous solution that involve ionic reactants or products may be represented more realistically by complete ionic equations and, more succinctly, by net ionic equations.

Chemistry End of Chapter Exercises

Exercise:

Problem:

What does it mean to say an equation is balanced? Why is it important for an equation to be balanced?

Solution:

An equation is balanced when the same number of each element is represented on the reactant and product sides. Equations must be balanced to accurately reflect the law of conservation of matter.

Exercise:

Problem: Consider molecular, complete ionic, and net ionic equations.

- What is the difference between these types of equations?
- In what circumstance would the complete and net ionic equations for a reaction be identical?

Exercise:

Problem: Balance the following equations:

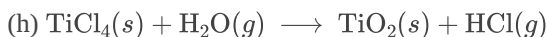
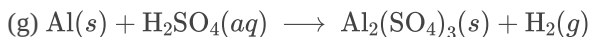
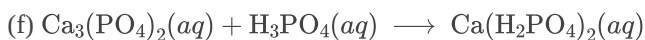
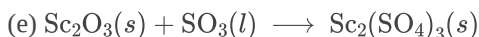
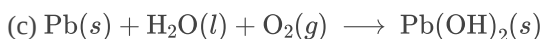
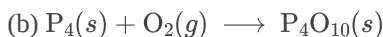
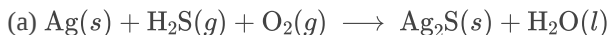
- $\text{PCl}_5(s) + \text{H}_2\text{O}(l) \longrightarrow \text{POCl}_3(l) + \text{HCl}(aq)$
- $\text{Cu}(s) + \text{HNO}_3(aq) \longrightarrow \text{Cu}(\text{NO}_3)_2(aq) + \text{H}_2\text{O}(l) + \text{NO}(g)$
- $\text{H}_2(g) + \text{I}_2(s) \longrightarrow \text{HI}(s)$
- $\text{Fe}(s) + \text{O}_2(g) \longrightarrow \text{Fe}_2\text{O}_3(s)$
- $\text{Na}(s) + \text{H}_2\text{O}(l) \longrightarrow \text{NaOH}(aq) + \text{H}_2(g)$
- $(\text{NH}_4)_2\text{Cr}_2\text{O}_7(s) \longrightarrow \text{Cr}_2\text{O}_3(s) + \text{N}_2(g) + \text{H}_2\text{O}(g)$
- $\text{P}_4(s) + \text{Cl}_2(g) \longrightarrow \text{PCl}_3(l)$
- $\text{PtCl}_4(s) \longrightarrow \text{Pt}(s) + \text{Cl}_2(g)$

Solution:

(a) $\text{PCl}_5(s) + \text{H}_2\text{O}(l) \longrightarrow \text{POCl}_3(l) + 2\text{HCl}(aq)$; (b) $3\text{Cu}(s) + 8\text{HNO}_3(aq) \longrightarrow 3\text{Cu}(\text{NO}_3)_2(aq) + 4\text{H}_2\text{O}(l) + 2\text{NO}(g)$; (c) $\text{H}_2(g) + \text{I}_2(s) \longrightarrow 2\text{HI}(s)$; (d) $4\text{Fe}(s) + 3\text{O}_2(g) \longrightarrow 2\text{Fe}_2\text{O}_3(s)$; (e) $2\text{Na}(s) + 2\text{H}_2\text{O}(l) \longrightarrow 2\text{NaOH}(aq) + \text{H}_2(g)$; (f) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7(s) \longrightarrow \text{Cr}_2\text{O}_3(s) + \text{N}_2(g) + 4\text{H}_2\text{O}(g)$; (g) $\text{P}_4(s) + 6\text{Cl}_2(g) \longrightarrow 4\text{PCl}_3(l)$; (h) $\text{PtCl}_4(s) \longrightarrow \text{Pt}(s) + 2\text{Cl}_2(g)$

Exercise:

Problem: Balance the following equations:

**Exercise:**

Problem: Write a balanced molecular equation describing each of the following chemical reactions.

(a) Solid calcium carbonate is heated and decomposes to solid calcium oxide and carbon dioxide gas.

(b) Gaseous butane, C_4H_{10} , reacts with diatomic oxygen gas to yield gaseous carbon dioxide and water vapor.

(c) Aqueous solutions of magnesium chloride and sodium hydroxide react to produce solid magnesium hydroxide and aqueous sodium chloride.

(d) Water vapor reacts with sodium metal to produce solid sodium hydroxide and hydrogen gas.

Solution:

(a) $\text{CaCO}_3(s) \longrightarrow \text{CaO}(s) + \text{CO}_2(g)$; (b) $2\text{C}_4\text{H}_{10}(g) + 13\text{O}_2(g) \longrightarrow 8\text{CO}_2(g) + 10\text{H}_2\text{O}(g)$; (c) $\text{MgCl}_2(aq) + 2\text{NaOH}(aq) \longrightarrow \text{Mg}(\text{OH})_2(s) + 2\text{NaCl}(aq)$; (d) $2\text{H}_2\text{O}(g) + 2\text{Na}(s) \longrightarrow 2\text{NaOH}(s) + \text{H}_2(g)$

Exercise:

Problem: Write a balanced equation describing each of the following chemical reactions.

(a) Solid potassium chlorate, KClO_3 , decomposes to form solid potassium chloride and diatomic oxygen gas.

(b) Solid aluminum metal reacts with solid diatomic iodine to form solid Al_2I_6 .

(c) When solid sodium chloride is added to aqueous sulfuric acid, hydrogen chloride gas and aqueous sodium sulfate are produced.

(d) Aqueous solutions of phosphoric acid and potassium hydroxide react to produce aqueous potassium dihydrogen phosphate and liquid water.

Exercise:

Problem:

Colorful fireworks often involve the decomposition of barium nitrate and potassium chlorate and the reaction of the metals magnesium, aluminum, and iron with oxygen.

(a) Write the formulas of barium nitrate and potassium chlorate.

(b) The decomposition of solid potassium chlorate leads to the formation of solid potassium chloride and diatomic oxygen gas. Write an equation for the reaction.

(c) The decomposition of solid barium nitrate leads to the formation of solid barium oxide, diatomic nitrogen gas, and diatomic oxygen gas. Write an equation for the reaction.

(d) Write separate equations for the reactions of the solid metals magnesium, aluminum, and iron with diatomic oxygen gas to yield the corresponding metal oxides. (Assume the iron oxide contains Fe^{3+} ions.)

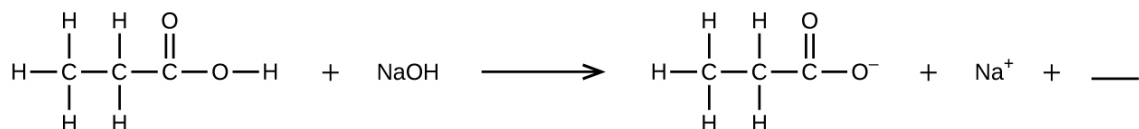
Solution:

(a) $\text{Ba}(\text{NO}_3)_2$, KClO_3 ; (b) $2\text{KClO}_3(s) \rightarrow 2\text{KCl}(s) + 3\text{O}_2(g)$; (c)
 $2\text{Ba}(\text{NO}_3)_2(s) \rightarrow 2\text{BaO}(s) + 2\text{N}_2(g) + 5\text{O}_2(g)$; (d) $2\text{Mg}(s) + \text{O}_2(g) \rightarrow 2\text{MgO}(s)$;
 $4\text{Al}(s) + 3\text{O}_2(g) \rightarrow 2\text{Al}_2\text{O}_3(s)$; $4\text{Fe}(s) + 3\text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s)$

Exercise:

Problem:

Fill in the blank with a single chemical formula for a covalent compound that will balance the equation:



Exercise:

Problem:

Aqueous hydrogen fluoride (hydrofluoric acid) is used to etch glass and to analyze minerals for their silicon content. Hydrogen fluoride will also react with sand (silicon dioxide).

(a) Write an equation for the reaction of solid silicon dioxide with hydrofluoric acid to yield gaseous silicon tetrafluoride and liquid water.

(b) The mineral fluorite (calcium fluoride) occurs extensively in Illinois. Solid calcium fluoride can also be prepared by the reaction of aqueous solutions of calcium chloride and sodium fluoride, yielding aqueous sodium chloride as the other product. Write complete and net ionic equations for this reaction.

Solution:

(a) $4\text{HF}(aq) + \text{SiO}_2(s) \rightarrow \text{SiF}_4(g) + 2\text{H}_2\text{O}(l)$; (b) complete ionic equation:
 $2\text{Na}^+(aq) + 2\text{F}^-(aq) + \text{Ca}^{2+}(aq) + 2\text{Cl}^-(aq) \rightarrow \text{CaF}_2(s) + 2\text{Na}^+(aq) + 2\text{Cl}^-(aq)$, net ionic
equation: $2\text{F}^-(aq) + \text{Ca}^{2+}(aq) \rightarrow \text{CaF}_2(s)$

Exercise:

Problem:

A novel process for obtaining magnesium from sea water involves several reactions. Write a balanced chemical equation for each step of the process.

(a) The first step is the decomposition of solid calcium carbonate from seashells to form solid calcium oxide and gaseous carbon dioxide.

(b) The second step is the formation of solid calcium hydroxide as the only product from the reaction of the solid calcium oxide with liquid water.

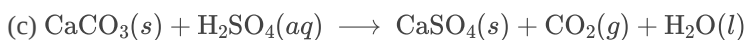
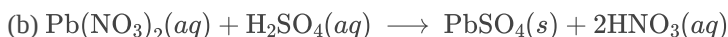
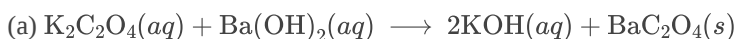
(c) Solid calcium hydroxide is then added to the seawater, reacting with dissolved magnesium chloride to yield solid magnesium hydroxide and aqueous calcium chloride.

(d) The solid magnesium hydroxide is added to a hydrochloric acid solution, producing dissolved magnesium chloride and liquid water.

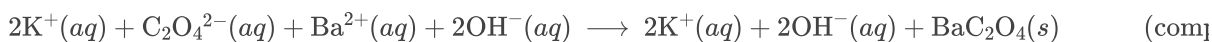
(e) Finally, the magnesium chloride is melted and electrolyzed to yield liquid magnesium metal and diatomic chlorine gas.

Exercise:**Problem:**

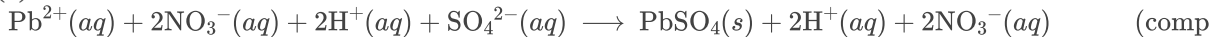
From the balanced molecular equations, write the complete ionic and net ionic equations for the following:

**Solution:**

(a)



(b)

**Glossary**

balanced equation

chemical equation with equal numbers of atoms for each element in the reactant and product

chemical equation

symbolic representation of a chemical reaction

coefficient

number placed in front of symbols or formulas in a chemical equation to indicate their relative amount

complete ionic equation

chemical equation in which all dissolved ionic reactants and products, including spectator ions, are explicitly represented by formulas for their dissociated ions

molecular equation

chemical equation in which all reactants and products are represented as neutral substances

net ionic equation

chemical equation in which only those dissolved ionic reactants and products that undergo a chemical or physical change are represented (excludes spectator ions)

product

substance formed by a chemical or physical change; shown on the right side of the arrow in a chemical equation

reactant

substance undergoing a chemical or physical change; shown on the left side of the arrow in a chemical equation

spectator ion

ion that does not undergo a chemical or physical change during a reaction, but its presence is required to maintain charge neutrality

Reaction Stoichiometry

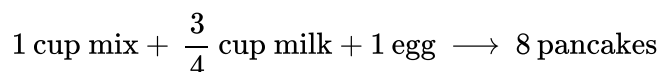
By the end of this section, you will be able to:

- Explain the concept of stoichiometry as it pertains to chemical reactions
- Use balanced chemical equations to derive stoichiometric factors relating amounts of reactants and products
- Perform stoichiometric calculations involving mass, moles, and solution molarity

A balanced chemical equation provides a great deal of information in a very succinct format. Chemical formulas provide the identities of the reactants and products involved in the chemical change, allowing classification of the reaction. Coefficients provide the relative numbers of these chemical species, allowing a quantitative assessment of the relationships between the amounts of substances consumed and produced by the reaction. These quantitative relationships are known as the reaction's **stoichiometry**, a term derived from the Greek words *stoicheion* (meaning “element”) and *metron* (meaning “measure”). In this module, the use of balanced chemical equations for various stoichiometric applications is explored.

The general approach to using stoichiometric relationships is similar in concept to the way people go about many common activities. Food preparation, for example, offers an appropriate comparison. A recipe for making eight pancakes calls for 1 cup pancake mix, $\frac{3}{4}$ cup milk, and one egg. The “equation” representing the preparation of pancakes per this recipe is

Equation:



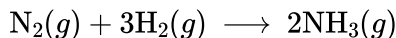
If two dozen pancakes are needed for a big family breakfast, the ingredient amounts must be increased proportionally according to the amounts given in the recipe. For example, the number of eggs required to make 24 pancakes is

Equation:

$$24 \text{ ~~pancakes~~} \times \frac{1 \text{ egg}}{8 \text{ ~~pancakes~~}} = 3 \text{ eggs}$$

Balanced chemical equations are used in much the same fashion to determine the amount of one reactant required to react with a given amount of another reactant, or to yield a given amount of product, and so forth. The coefficients in the balanced equation are used to derive **stoichiometric factors** that permit computation of the desired quantity. To illustrate this idea, consider the production of ammonia by reaction of hydrogen and nitrogen:

Equation:



This equation shows ammonia molecules are produced from hydrogen molecules in a 2:3 ratio, and stoichiometric factors may be derived using any amount (number) unit:

Equation:

$$\frac{2 \text{ NH}_3 \text{ molecules}}{3 \text{ H}_2 \text{ molecules}} \text{ or } \frac{2 \text{ doz NH}_3 \text{ molecules}}{3 \text{ doz H}_2 \text{ molecules}} \text{ or } \frac{2 \text{ mol NH}_3 \text{ molecules}}{3 \text{ mol H}_2 \text{ molecules}}$$

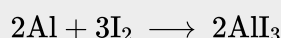
These stoichiometric factors can be used to compute the number of ammonia molecules produced from a given number of hydrogen molecules, or the number of hydrogen molecules required to produce a given number of ammonia molecules. Similar factors may be derived for any pair of substances in any chemical equation.

Example:

Moles of Reactant Required in a Reaction

How many moles of I_2 are required to react with 0.429 mol of Al according to the following equation (see [link](#))?

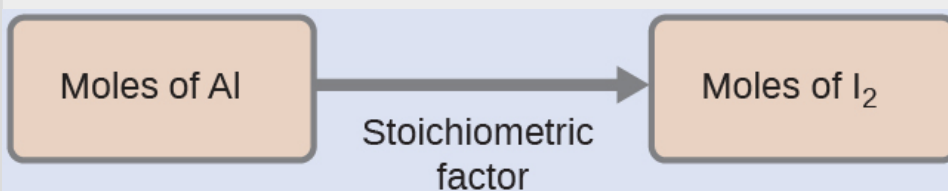
Equation:



Aluminum and iodine react to produce aluminum iodide. The heat of the reaction vaporizes some of the solid iodine as a purple vapor. (credit: modification of work by Mark Ott)

Solution

Referring to the balanced chemical equation, the stoichiometric factor relating the two substances of interest is $\frac{3 \text{ mol } I_2}{2 \text{ mol } Al}$. The molar amount of iodine is derived by multiplying the provided molar amount of aluminum by this factor:



Equation:

$$\begin{aligned} \text{mol } I_2 &= 0.429 \cancel{\text{mol Al}} \times \frac{3 \text{ mol } I_2}{2 \cancel{\text{mol Al}}} \\ &= 0.644 \text{ mol } I_2 \end{aligned}$$

Check Your Learning

How many moles of $Ca(OH)_2$ are required to react with 1.36 mol of H_3PO_4 to produce $Ca_3(PO_4)_2$ according to the equation $3Ca(OH)_2 + 2H_3PO_4 \longrightarrow Ca_3(PO_4)_2 + 6H_2O$?

Note:

Answer:

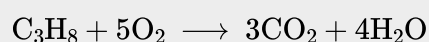
2.04 mol

Example:

Number of Product Molecules Generated by a Reaction

How many carbon dioxide molecules are produced when 0.75 mol of propane is combusted according to this equation?

Equation:



Solution

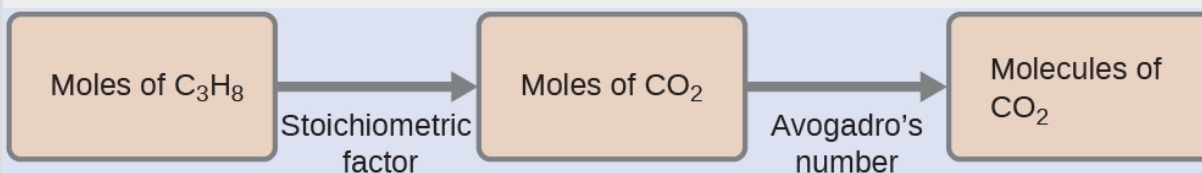
The approach here is the same as for [\[link\]](#), though the absolute number of molecules is requested, not the number of moles of molecules. This will simply require use of the moles-to-numbers conversion factor, Avogadro's number.

The balanced equation shows that carbon dioxide is produced from propane in a 3:1 ratio:

Equation:

$$\frac{3 \text{ mol CO}_2}{1 \text{ mol C}_3\text{H}_8}$$

Using this stoichiometric factor, the provided molar amount of propane, and Avogadro's number,



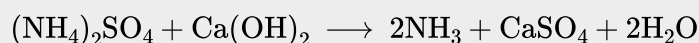
Equation:

$$0.75 \text{ mol C}_3\text{H}_8 \times \frac{3 \text{ mol CO}_2}{1 \text{ mol C}_3\text{H}_8} \times \frac{6.022 \times 10^{23} \text{ CO}_2 \text{ molecules}}{1 \text{ mol CO}_2} = 1.4 \times 10^{24} \text{ CO}_2 \text{ molecules}$$

Check Your Learning

How many NH_3 molecules are produced by the reaction of 4.0 mol of Ca(OH)_2 according to the following equation:

Equation:



Note:

Answer:

4.8×10^{24} NH_3 molecules

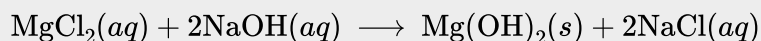
These examples illustrate the ease with which the amounts of substances involved in a chemical reaction of known stoichiometry may be related. Directly measuring numbers of atoms and molecules is, however, not an easy task, and the practical application of stoichiometry requires that we use the more readily measured property of mass.

Example:

Relating Masses of Reactants and Products

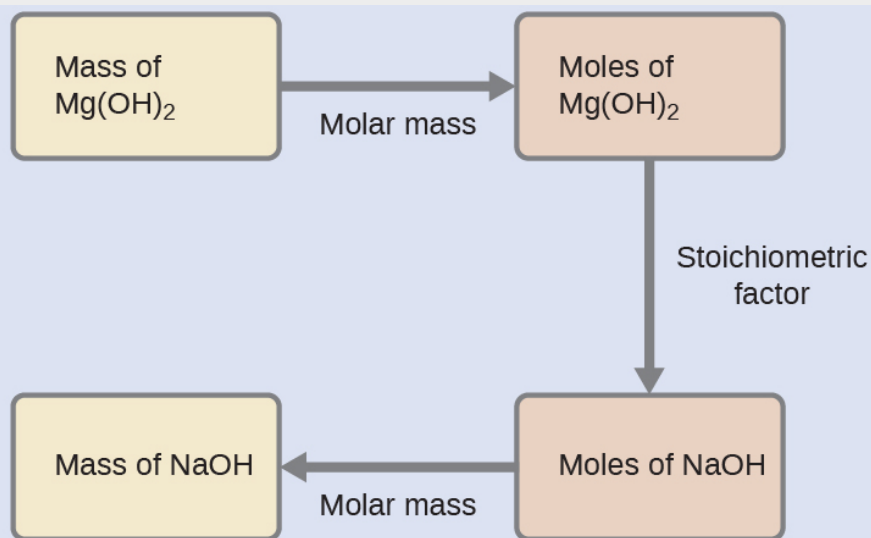
What mass of sodium hydroxide, NaOH , would be required to produce 16 g of the antacid milk of magnesia [magnesium hydroxide, $\text{Mg}(\text{OH})_2$] by the following reaction?

Equation:



Solution

The approach used previously in [\[link\]](#) and [\[link\]](#) is likewise used here; that is, we must derive an appropriate stoichiometric factor from the balanced chemical equation and use it to relate the amounts of the two substances of interest. In this case, however, masses (not molar amounts) are provided and requested, so additional steps of the sort learned in the previous chapter are required. The calculations required are outlined in this flowchart:



Equation:

$$16 \text{ g Mg}(\text{OH})_2 \times \frac{1 \text{ mol Mg}(\text{OH})_2}{58.3 \text{ g Mg}(\text{OH})_2} \times \frac{2 \text{ mol NaOH}}{1 \text{ mol Mg}(\text{OH})_2} \times \frac{40.0 \text{ g NaOH}}{1 \text{ mol NaOH}} = 22 \text{ g NaOH}$$

Check Your Learning

What mass of gallium oxide, Ga_2O_3 , can be prepared from 29.0 g of gallium metal? The equation for the reaction is $4\text{Ga} + 3\text{O}_2 \longrightarrow 2\text{Ga}_2\text{O}_3$.

Note:

Answer:

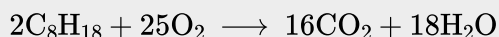
39.0 g

Example:

Relating Masses of Reactants

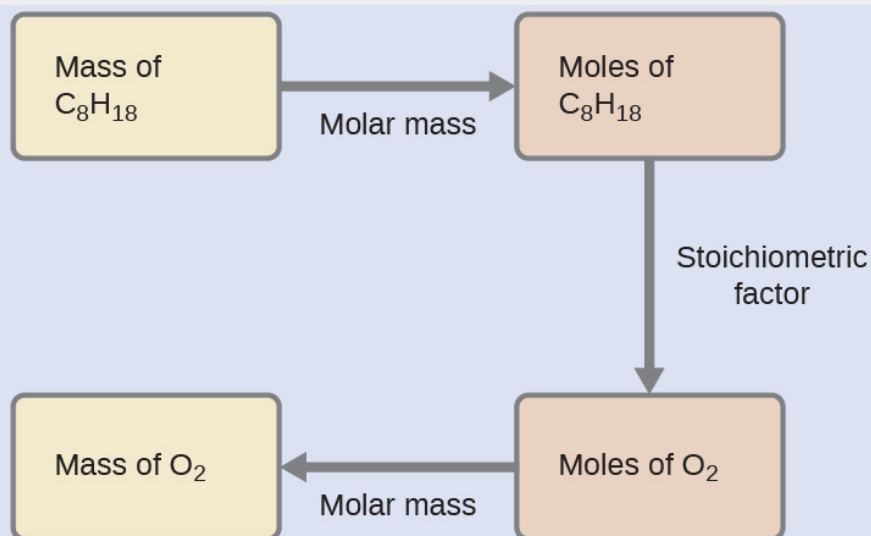
What mass of oxygen gas, O_2 , from the air is consumed in the combustion of 702 g of octane, C_8H_{18} , one of the principal components of gasoline?

Equation:



Solution

The approach required here is the same as for the [link](#), differing only in that the provided and requested masses are both for reactant species.



Equation:

$$702 \text{ g C}_8\text{H}_{18} \times \frac{1 \text{ mol C}_8\text{H}_{18}}{114.23 \text{ g C}_8\text{H}_{18}} \times \frac{25 \text{ mol O}_2}{2 \text{ mol C}_8\text{H}_{18}} \times \frac{32.00 \text{ g O}_2}{\text{mol O}_2} = 2.46 \times 10^3 \text{ g O}_2$$

Check Your Learning

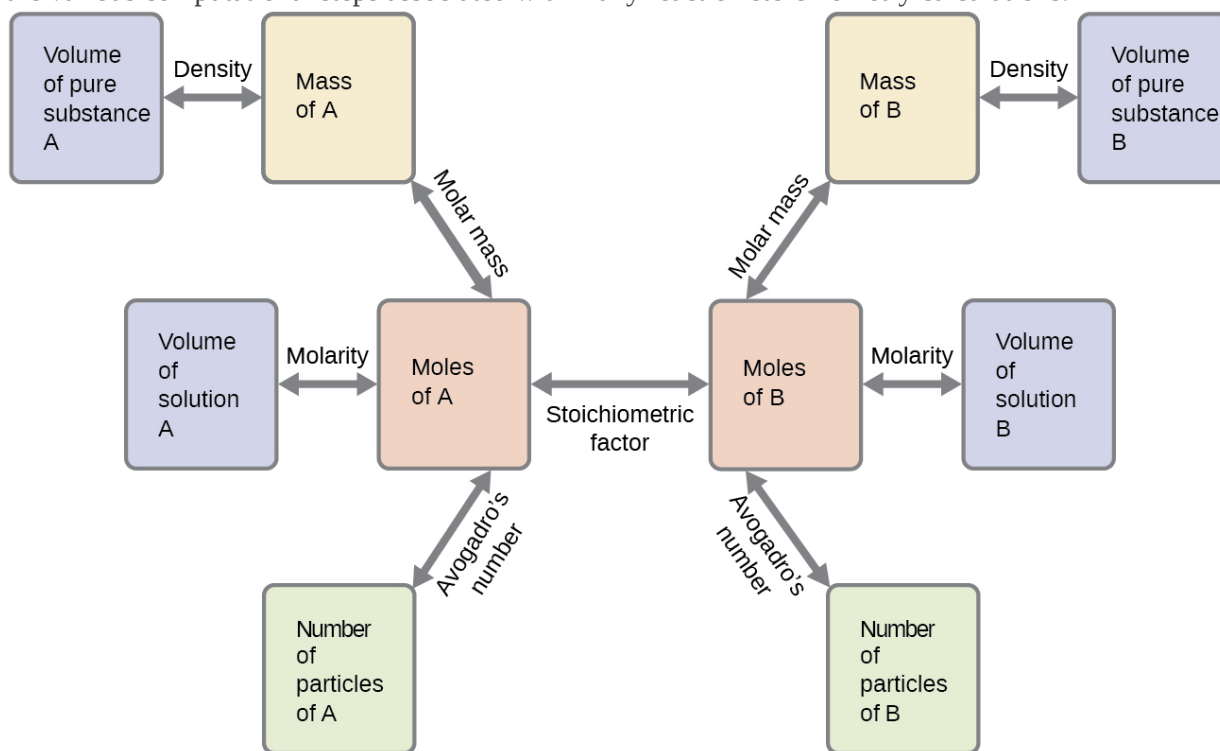
What mass of CO is required to react with 25.13 g of Fe_2O_3 according to the equation $\text{Fe}_2\text{O}_3 + 3\text{CO} \longrightarrow 2\text{Fe} + 3\text{CO}_2$?

Note:

Answer:

13.22 g

These examples illustrate just a few instances of reaction stoichiometry calculations. Numerous variations on the beginning and ending computational steps are possible depending upon what particular quantities are provided and sought (volumes, solution concentrations, and so forth). Regardless of the details, all these calculations share a common essential component: the use of stoichiometric factors derived from balanced chemical equations. [\[link\]](#) provides a general outline of the various computational steps associated with many reaction stoichiometry calculations.



The flowchart depicts the various computational steps involved in most reaction stoichiometry calculations.

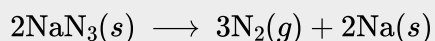
Note:

Airbags

Airbags ([\[link\]](#)) are a safety feature provided in most automobiles since the 1990s. The effective operation of an airbag requires that it be rapidly inflated with an appropriate amount (volume) of gas when the vehicle is involved in a collision. This requirement is satisfied in many automotive airbag systems through use of explosive chemical reactions, one common choice being the decomposition of

sodium azide, NaN_3 . When sensors in the vehicle detect a collision, an electrical current is passed through a carefully measured amount of NaN_3 to initiate its decomposition:

Equation:



This reaction is very rapid, generating gaseous nitrogen that can deploy and fully inflate a typical airbag in a fraction of a second ($\sim 0.03\text{--}0.1$ s). Among many engineering considerations, the amount of sodium azide used must be appropriate for generating enough nitrogen gas to fully inflate the air bag and ensure its proper function. For example, a small mass (~ 100 g) of NaN_3 will generate approximately 50 L of N_2 .



Airbags deploy upon impact to minimize serious injuries to passengers.
(credit: Jon Seidman)

Key Concepts and Summary

A balanced chemical equation may be used to describe a reaction's stoichiometry (the relationships between amounts of reactants and products). Coefficients from the equation are used to derive stoichiometric factors that subsequently may be used for computations relating reactant and product masses, molar amounts, and other quantitative properties.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Write the balanced equation, then outline the steps necessary to determine the information requested in each of the following:

- (a) The number of moles and the mass of chlorine, Cl_2 , required to react with 10.0 g of sodium metal, Na, to produce sodium chloride, NaCl.
- (b) The number of moles and the mass of oxygen formed by the decomposition of 1.252 g of mercury(II) oxide.
- (c) The number of moles and the mass of sodium nitrate, NaNO_3 , required to produce 128 g of oxygen. (NaNO_2 is the other product.)
- (d) The number of moles and the mass of carbon dioxide formed by the combustion of 20.0 kg of carbon in an excess of oxygen.
- (e) The number of moles and the mass of copper(II) carbonate needed to produce 1.500 kg of copper(II) oxide. (CO_2 is the other product.)
- (f)

The number of moles and the mass of $\text{Br}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\text{Br}$ formed by the reaction of 12.85 g of $\text{H}_2\text{C}=\text{CH}_2$ with an excess of Br_2 .

Exercise:

Problem: Determine the number of moles and the mass requested for each reaction in [\[link\]](#).

Solution:

(a) 0.435 mol Na, 0.217 mol Cl_2 , 15.4 g Cl_2 ; (b) 0.005780 mol HgO , 2.890×10^{-3} mol O_2 , 9.248×10^{-2} g O_2 ; (c) 8.00 mol NaNO_3 , 6.8×10^2 g NaNO_3 ; (d) 1665 mol CO_2 , 73.3 kg CO_2 ; (e) 18.86 mol CuO , 2.330 kg CuCO_3 ; (f) 0.4580 mol $\text{C}_2\text{H}_4\text{Br}_2$, 86.05 g $\text{C}_2\text{H}_4\text{Br}_2$

Exercise:**Problem:**

Write the balanced equation, then outline the steps necessary to determine the information requested in each of the following:

- (a) The number of moles and the mass of Mg required to react with 5.00 g of HCl and produce MgCl_2 and H_2 .
- (b) The number of moles and the mass of oxygen formed by the decomposition of 1.252 g of silver(I) oxide.

- (c) The number of moles and the mass of magnesium carbonate, MgCO_3 , required to produce 283 g of carbon dioxide. (MgO is the other product.)
- (d) The number of moles and the mass of water formed by the combustion of 20.0 kg of acetylene, C_2H_2 , in an excess of oxygen.
- (e) The number of moles and the mass of barium peroxide, BaO_2 , needed to produce 2.500 kg of barium oxide, BaO (O_2 is the other product.)
- (f)

The number of moles and the mass of $\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C} = \text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$ required to react with H_2O to produce 9.55 g of $\begin{array}{c} \text{H} & \text{H} \\ | & | \\ \text{H}-\text{C}- & \text{C}-\text{O}-\text{H} \\ | & | \\ \text{H} & \text{H} \end{array}$.

Exercise:

Problem: Determine the number of moles and the mass requested for each reaction in [\[link\]](#).

Solution:

(a) 0.0686 mol Mg , 1.67 g Mg ; (b) 2.701×10^{-3} mol O_2 , 0.08644 g O_2 ; (c) 6.43 mol MgCO_3 , 542 g MgCO_3 (d) 713 mol H_2O , 12.8 kg H_2O ; (e) 16.31 mol BaO_2 , 2762 g BaO_2 ; (f) 0.207 mol C_2H_4 , 5.81 g C_2H_4

Exercise:

Problem:

H_2 is produced by the reaction of 118.5 mL of a 0.8775-M solution of H_3PO_4 according to the following equation: $2\text{Cr} + 2\text{H}_3\text{PO}_4 \longrightarrow 3\text{H}_2 + 2\text{CrPO}_4$.

- (a) Outline the steps necessary to determine the number of moles and mass of H_2 .
- (b) Perform the calculations outlined.

Exercise:

Problem:

Gallium chloride is formed by the reaction of 2.6 L of a 1.44 M solution of HCl according to the following equation: $2\text{Ga} + 6\text{HCl} \longrightarrow 2\text{GaCl}_3 + 3\text{H}_2$.

- (a) Outline the steps necessary to determine the number of moles and mass of gallium chloride.
- (b) Perform the calculations outlined.

Solution:

(a) volume HCl solution \longrightarrow mol HCl \longrightarrow mol GaCl_3 ; (b) 1.25 mol GaCl_3 , 2.2×10^2 g GaCl_3

Exercise:

Problem:

I₂ is produced by the reaction of 0.4235 mol of CuCl₂ according to the following equation:
$$2\text{CuCl}_2 + 4\text{KI} \longrightarrow 2\text{CuI} + 4\text{KCl} + \text{I}_2.$$

(a) How many molecules of I₂ are produced?

(b) What mass of I₂ is produced?

Exercise:**Problem:**

Silver is often extracted from ores such as K[Ag(CN)₂] and then recovered by the reaction
$$2\text{K}[\text{Ag}(\text{CN})_2](aq) + \text{Zn}(s) \longrightarrow 2\text{Ag}(s) + \text{Zn}(\text{CN})_2(aq) + 2\text{KCN}(aq)$$

(a) How many molecules of Zn(CN)₂ are produced by the reaction of 35.27 g of K[Ag(CN)₂]?

(b) What mass of Zn(CN)₂ is produced?

Solution:

(a) 5.337×10^{22} molecules; (b) 10.41 g Zn(CN)₂

Exercise:**Problem:**

What mass of silver oxide, Ag₂O, is required to produce 25.0 g of silver sulfadiazine, AgC₁₀H₉N₄SO₂, from the reaction of silver oxide and sulfadiazine?
$$2\text{C}_{10}\text{H}_{10}\text{N}_4\text{SO}_2 + \text{Ag}_2\text{O} \longrightarrow 2\text{AgC}_{10}\text{H}_9\text{N}_4\text{SO}_2 + \text{H}_2\text{O}$$

Exercise:**Problem:**

Carborundum is silicon carbide, SiC, a very hard material used as an abrasive on sandpaper and in other applications. It is prepared by the reaction of pure sand, SiO₂, with carbon at high temperature. Carbon monoxide, CO, is the other product of this reaction. Write the balanced equation for the reaction, and calculate how much SiO₂ is required to produce 3.00 kg of SiC.

Solution:

$$\text{SiO}_2 + 3\text{C} \longrightarrow \text{SiC} + 2\text{CO}, 4.50 \text{ kg SiO}_2$$

Exercise:**Problem:**

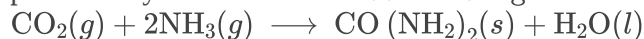
Automotive air bags inflate when a sample of sodium azide, NaN₃, is very rapidly decomposed.
$$2\text{NaN}_3(s) \longrightarrow 2\text{Na}(s) + 3\text{N}_2(g)$$

What mass of sodium azide is required to produce 2.6 ft³ (73.6 L) of nitrogen gas with a density of 1.25 g/L?

Exercise:

Problem:

Urea, $\text{CO}(\text{NH}_2)_2$, is manufactured on a large scale for use in producing urea-formaldehyde plastics and as a fertilizer. What is the maximum mass of urea that can be manufactured from the CO_2 produced by combustion of $1.00 \times 10^3 \text{ kg}$ of carbon followed by the reaction?

**Solution:**

$$5.00 \times 10^3 \text{ kg}$$

Exercise:**Problem:**

In an accident, a solution containing 2.5 kg of nitric acid was spilled. Two kilograms of Na_2CO_3 was quickly spread on the area and CO_2 was released by the reaction. Was sufficient Na_2CO_3 used to neutralize all of the acid?

Exercise:**Problem:**

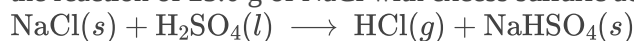
A compact car gets 37.5 miles per gallon on the highway. If gasoline contains 84.2% carbon by mass and has a density of 0.8205 g/mL, determine the mass of carbon dioxide produced during a 500-mile trip (3.785 liters per gallon).

Solution:

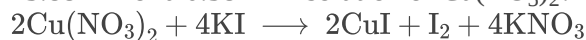
$$1.28 \times 10^5 \text{ g CO}_2$$

Exercise:**Problem:**

What volume of 0.750 M hydrochloric acid solution can be prepared from the HCl produced by the reaction of 25.0 g of NaCl with excess sulfuric acid?

**Exercise:****Problem:**

What volume of a 0.2089 M KI solution contains enough KI to react exactly with the $\text{Cu}(\text{NO}_3)_2$ in 43.88 mL of a 0.3842 M solution of $\text{Cu}(\text{NO}_3)_2$?

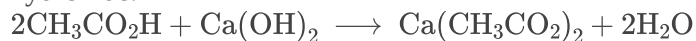
**Solution:**

$$161.40 \text{ mL KI solution}$$

Exercise:

Problem:

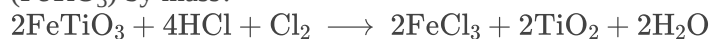
A mordant is a substance that combines with a dye to produce a stable fixed color in a dyed fabric. Calcium acetate is used as a mordant. It is prepared by the reaction of acetic acid with calcium hydroxide.



What mass of $\text{Ca}(\text{OH})_2$ is required to react with the acetic acid in 25.0 mL of a solution having a density of 1.065 g/mL and containing 58.0% acetic acid by mass?

Exercise:**Problem:**

The toxic pigment called white lead, $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$, has been replaced in white paints by rutile, TiO_2 . How much rutile (g) can be prepared from 379 g of an ore that contains 88.3% ilmenite (FeTiO_3) by mass?

**Solution:**

176 g TiO_2

Glossary

stoichiometric factor

ratio of coefficients in a balanced chemical equation, used in computations relating amounts of reactants and products

stoichiometry

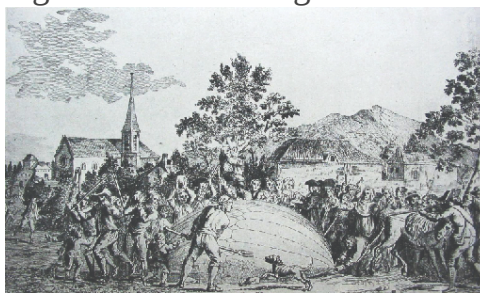
relationships between the amounts of reactants and products of a chemical reaction

Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law

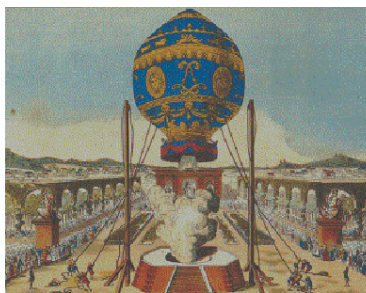
By the end of this section, you will be able to:

- Identify the mathematical relationships between the various properties of gases
- Use the ideal gas law, and related gas laws, to compute the values of various gas properties under specified conditions

During the seventeenth and especially eighteenth centuries, driven both by a desire to understand nature and a quest to make balloons in which they could fly ([\[link\]](#)), a number of scientists established the relationships between the macroscopic physical properties of gases, that is, pressure, volume, temperature, and amount of gas. Although their measurements were not precise by today's standards, they were able to determine the mathematical relationships between pairs of these variables (e.g., pressure and temperature, pressure and volume) that hold for an *ideal* gas—a hypothetical construct that real gases approximate under certain conditions. Eventually, these individual laws were combined into a single equation—the *ideal gas law*—that relates gas quantities for gases and is quite accurate for low pressures and moderate temperatures. We will consider the key developments in individual relationships (for pedagogical reasons not quite in historical order), then put them together in the ideal gas law.



(a)



(b)



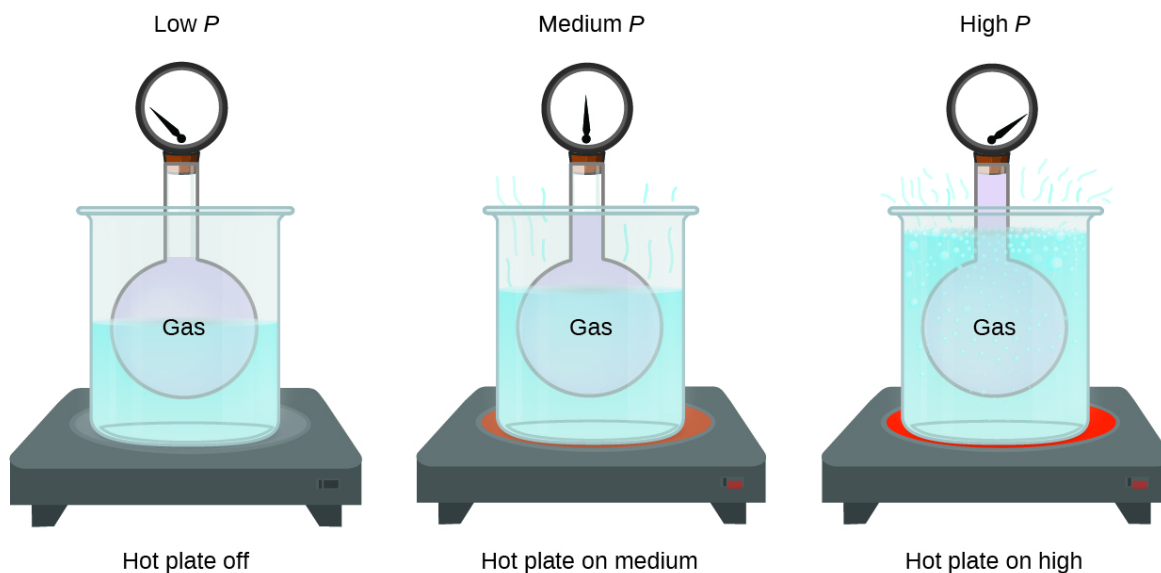
(c)

In 1783, the first (a) hydrogen-filled balloon flight, (b) manned hot air balloon flight, and (c) manned hydrogen-filled balloon flight occurred. When the hydrogen-filled balloon depicted in (a) landed, the frightened villagers of Gonesse reportedly destroyed it with pitchforks and knives. The launch of the latter was reportedly viewed by 400,000 people in Paris.

Pressure and Temperature: Amontons's Law

Imagine filling a rigid container attached to a pressure gauge with gas and then sealing the container so that no gas may escape. If the container is cooled, the gas inside likewise gets colder and its pressure is observed to decrease. Since the container is

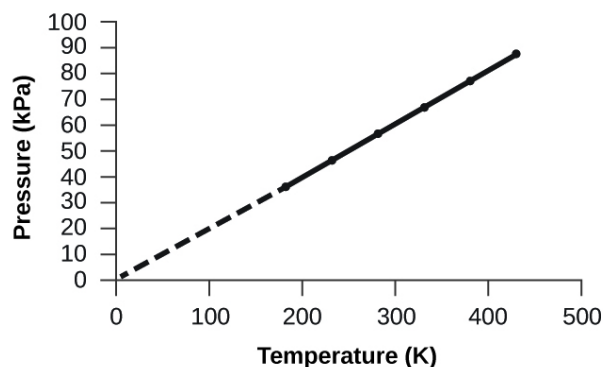
rigid and tightly sealed, both the volume and number of moles of gas remain constant. If we heat the sphere, the gas inside gets hotter ([\[link\]](#)) and the pressure increases.



The effect of temperature on gas pressure: When the hot plate is off, the pressure of the gas in the sphere is relatively low. As the gas is heated, the pressure of the gas in the sphere increases.

This relationship between temperature and pressure is observed for any sample of gas confined to a constant volume. An example of experimental pressure-temperature data is shown for a sample of air under these conditions in [\[link\]](#). We find that temperature and pressure are linearly related, and if the temperature is on the kelvin scale, then P and T are directly proportional (again, when *volume and moles of gas are held constant*); if the temperature on the kelvin scale increases by a certain factor, the gas pressure increases by the same factor.

Temperature (°C)	Temperature (K)	Pressure (kPa)
-150	173	36.0
-100	223	46.4
-50	273	56.7
0	323	67.1
50	373	77.5
100	423	88.0



For a constant volume and amount of air, the pressure and temperature are directly proportional, provided the temperature is in kelvin. (Measurements cannot be made at lower temperatures because of the condensation of the gas.) When this line is extrapolated to lower pressures, it reaches a pressure of 0 at -273°C , which is 0 on the kelvin scale and the lowest possible temperature, called absolute zero.

Guillaume Amontons was the first to empirically establish the relationship between the pressure and the temperature of a gas (~1700), and Joseph Louis Gay-Lussac determined the relationship more precisely (~1800). Because of this, the P - T relationship for gases is known as either **Amontons's law** or **Gay-Lussac's law**. Under either name, it states that *the pressure of a given amount of gas is directly proportional to its temperature on the kelvin scale when the volume is held constant*. Mathematically, this can be written:

Equation:

$$P \propto T \text{ or } P = \text{constant} \times T \text{ or } P = k \times T$$

where \propto means "is proportional to," and k is a proportionality constant that depends on the identity, amount, and volume of the gas.

For a confined, constant volume of gas, the ratio $\frac{P}{T}$ is therefore constant (i.e., $\frac{P}{T} = k$). If the gas is initially in "Condition 1" (with $P = P_1$ and $T = T_1$), and then changes to "Condition 2" (with $P = P_2$ and $T = T_2$), we have that $\frac{P_1}{T_1} = k$ and $\frac{P_2}{T_2} = k$, which reduces to $\frac{P_1}{T_1} = \frac{P_2}{T_2}$. This equation is useful for pressure-temperature calculations for a confined gas at constant volume. Note that temperatures must be on the kelvin scale for any gas law calculations (0 on the kelvin scale and the lowest possible temperature is called **absolute zero**). (Also note that there are at least three ways we can describe

how the pressure of a gas changes as its temperature changes: We can use a table of values, a graph, or a mathematical equation.)

Example:

Predicting Change in Pressure with Temperature

A can of hair spray is used until it is empty except for the propellant, isobutane gas.

(a) On the can is the warning “Store only at temperatures below 120 °F (48.8 °C). Do not incinerate.” Why?

(b) The gas in the can is initially at 24 °C and 360 kPa, and the can has a volume of 350 mL. If the can is left in a car that reaches 50 °C on a hot day, what is the new pressure in the can?

Solution

(a) The can contains an amount of isobutane gas at a constant volume, so if the temperature is increased by heating, the pressure will increase proportionately. High temperature could lead to high pressure, causing the can to burst. (Also, isobutane is combustible, so incineration could cause the can to explode.)

(b) We are looking for a pressure change due to a temperature change at constant volume, so we will use Amontons’s/Gay-Lussac’s law. Taking P_1 and T_1 as the initial values, T_2 as the temperature where the pressure is unknown and P_2 as the unknown pressure, and converting °C to K, we have:

Equation:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ which means that } \frac{360 \text{ kPa}}{297 \text{ K}} = \frac{P_2}{323 \text{ K}}$$

Rearranging and solving gives: $P_2 = \frac{360 \text{ kPa} \times 323 \text{ K}}{297 \text{ K}} = 390 \text{ kPa}$

Check Your Learning

A sample of nitrogen, N_2 , occupies 45.0 mL at 27 °C and 600 torr. What pressure will it have if cooled to –73 °C while the volume remains constant?

Note:

Answer:

400 torr

Volume and Temperature: Charles's Law

If we fill a balloon with air and seal it, the balloon contains a specific amount of air at atmospheric pressure, let's say 1 atm. If we put the balloon in a refrigerator, the gas inside gets cold and the balloon shrinks (although both the amount of gas and its pressure remain constant). If we make the balloon very cold, it will shrink a great deal, and it expands again when it warms up.

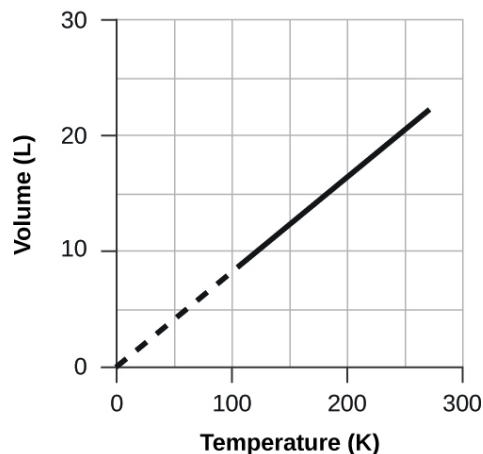
Note:



This [video](#) shows how cooling and heating a gas causes its volume to decrease or increase, respectively.

These examples of the effect of temperature on the volume of a given amount of a confined gas at constant pressure are true in general: The volume increases as the temperature increases, and decreases as the temperature decreases. Volume-temperature data for a 1-mole sample of methane gas at 1 atm are listed and graphed in [\[link\]](#).

Temperature (°C)	Temperature (K)	Volume (L)
-3	270	22
-23	250	21
-53	220	18
-162	111	9



The volume and temperature are linearly related for 1 mole of methane gas at a constant pressure of 1 atm. If the temperature is in kelvin, volume and temperature are directly proportional. The line stops at 111 K because methane liquefies at this temperature; when extrapolated, it intersects the graph's origin, representing a temperature of absolute zero.

The relationship between the volume and temperature of a given amount of gas at constant pressure is known as Charles's law in recognition of the French scientist and balloon flight pioneer Jacques Alexandre César Charles. **Charles's law** states that *the volume of a given amount of gas is directly proportional to its temperature on the kelvin scale when the pressure is held constant.*

Mathematically, this can be written as:

Equation:

$$V \propto T \text{ or } V = \text{constant} \cdot T \text{ or } V = k \cdot T \text{ or } V_1/T_1 = V_2/T_2$$

with k being a proportionality constant that depends on the amount and pressure of the gas.

For a confined, constant pressure gas sample, $\frac{V}{T}$ is constant (i.e., the ratio = k), and as seen with the P - T relationship, this leads to another form of Charles's law: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$.

Example:

Predicting Change in Volume with Temperature

A sample of carbon dioxide, CO_2 , occupies 0.300 L at 10 °C and 750 torr. What volume will the gas have at 30 °C and 750 torr?

Solution

Because we are looking for the volume change caused by a temperature change at constant pressure, this is a job for Charles's law. Taking V_1 and T_1 as the initial values, T_2 as the temperature at which the volume is unknown and V_2 as the unknown volume, and converting °C into K we have:

Equation:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which means that } \frac{0.300 \text{ L}}{283 \text{ K}} = \frac{V_2}{303 \text{ K}}$$

Rearranging and solving gives: $V_2 = \frac{0.300 \text{ L} \times 303 \text{ K}}{283 \text{ K}} = 0.321 \text{ L}$

This answer supports our expectation from Charles's law, namely, that raising the gas temperature (from 283 K to 303 K) at a constant pressure will yield an increase in its volume (from 0.300 L to 0.321 L).

Check Your Learning

A sample of oxygen, O_2 , occupies 32.2 mL at 30 °C and 452 torr. What volume will it occupy at –70 °C and the same pressure?

Note:

Answer:

21.6 mL

Example:

Measuring Temperature with a Volume Change

Temperature is sometimes measured with a gas thermometer by observing the change in the volume of the gas as the temperature changes at constant pressure. The hydrogen in a particular hydrogen gas thermometer has a volume of 150.0 cm³ when immersed in a mixture of ice and water (0.00 °C). When immersed in boiling liquid ammonia, the volume of the hydrogen, at the same pressure, is 131.7 cm³. Find the temperature of boiling ammonia on the kelvin and Celsius scales.

Solution

A volume change caused by a temperature change at constant pressure means we should use Charles's law. Taking V_1 and T_1 as the initial values, T_2 as the temperature at which the volume is unknown and V_2 as the unknown volume, and converting °C into K we have:

Equation:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which means that } \frac{150.0 \text{ cm}^3}{273.15 \text{ K}} = \frac{131.7 \text{ cm}^3}{T_2}$$

Rearrangement gives $T_2 = \frac{131.7 \text{ cm}^3 \times 273.15 \text{ K}}{150.0 \text{ cm}^3} = 239.8 \text{ K}$

Subtracting 273.15 from 239.8 K, we find that the temperature of the boiling ammonia on the Celsius scale is –33.4 °C.

Check Your Learning

What is the volume of a sample of ethane at 467 K and 1.1 atm if it occupies 405 mL at 298 K and 1.1 atm?

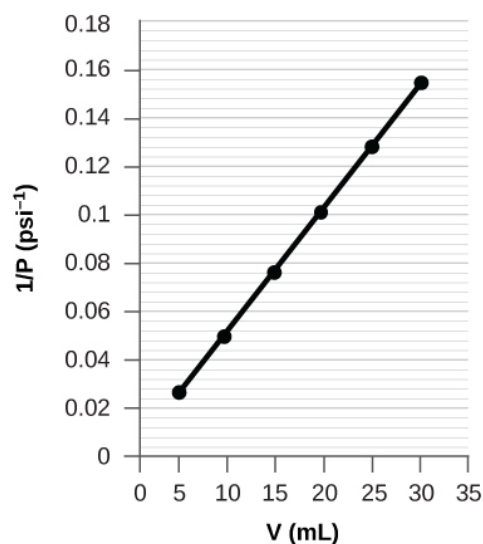
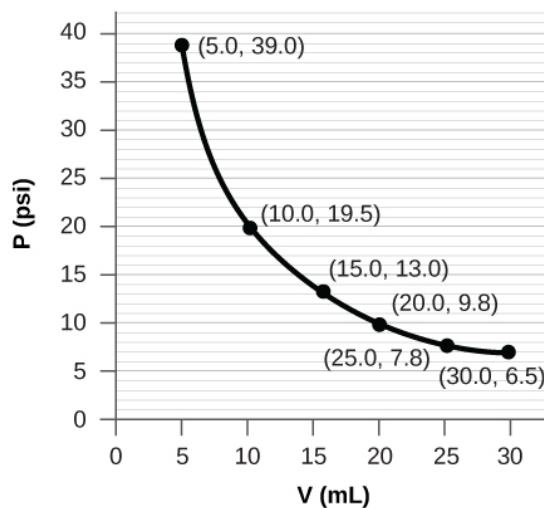
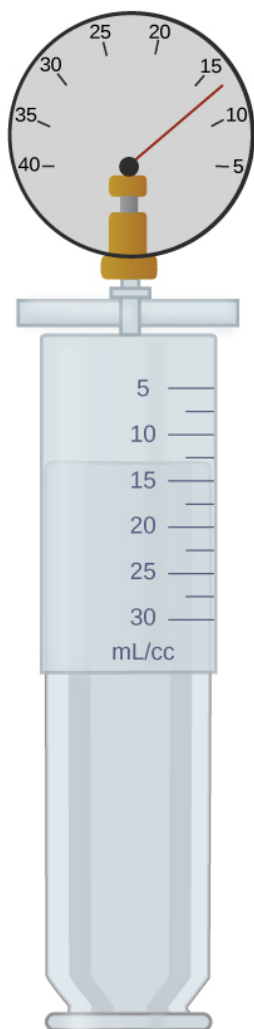
Note:

Answer:

635 mL

Volume and Pressure: Boyle's Law

If we partially fill an airtight syringe with air, the syringe contains a specific amount of air at constant temperature, say 25 °C. If we slowly push in the plunger while keeping temperature constant, the gas in the syringe is compressed into a smaller volume and its pressure increases; if we pull out the plunger, the volume increases and the pressure decreases. This example of the effect of volume on the pressure of a given amount of a confined gas is true in general. Decreasing the volume of a contained gas will increase its pressure, and increasing its volume will decrease its pressure. In fact, if the volume increases by a certain factor, the pressure decreases by the same factor, and vice versa. Volume-pressure data for an air sample at room temperature are graphed in [\[link\]](#).



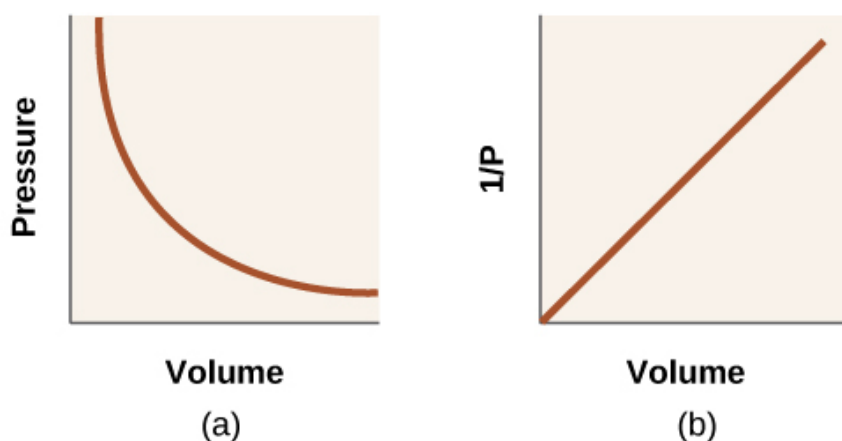
When a gas occupies a smaller volume, it exerts a higher pressure; when it occupies a larger volume, it exerts a lower pressure (assuming the amount of gas and the temperature do not change). Since P and V are inversely proportional, a graph of $\frac{1}{P}$ vs. V is linear.

Unlike the P - T and V - T relationships, pressure and volume are not directly proportional to each other. Instead, P and V exhibit inverse proportionality: Increasing the pressure results in a decrease of the volume of the gas. Mathematically this can be written:

Equation:

$$P \propto 1/V \text{ or } P = k \cdot 1/V \text{ or } P \cdot V = k \text{ or } P_1 V_1 = P_2 V_2$$

with k being a constant. Graphically, this relationship is shown by the straight line that results when plotting the inverse of the pressure ($\frac{1}{P}$) versus the volume (V), or the inverse of volume ($\frac{1}{V}$) versus the pressure (P). Graphs with curved lines are difficult to read accurately at low or high values of the variables, and they are more difficult to use in fitting theoretical equations and parameters to experimental data. For those reasons, scientists often try to find a way to “linearize” their data. If we plot P versus V , we obtain a hyperbola (see [\[link\]](#)).



The relationship between pressure and volume is inversely proportional. (a) The graph of P vs. V is a hyperbola, whereas (b) the graph of $(\frac{1}{P})$ vs. V is linear.

The relationship between the volume and pressure of a given amount of gas at constant temperature was first published by the English natural philosopher Robert Boyle over 300 years ago. It is summarized in the statement now known as **Boyle's law**: *The volume of a given amount of gas held at constant temperature is inversely proportional to the pressure under which it is measured.*

Example:

Volume of a Gas Sample

The sample of gas in [\[link\]](#) has a volume of 15.0 mL at a pressure of 13.0 psi. Determine the pressure of the gas at a volume of 7.5 mL, using:

(a) the P - V graph in [\[link\]](#)

(b) the $\frac{1}{P}$ vs. V graph in [\[link\]](#)

(c) the Boyle's law equation

Comment on the likely accuracy of each method.

Solution

(a) Estimating from the P - V graph gives a value for P somewhere around 27 psi.

(b) Estimating from the $\frac{1}{P}$ versus V graph give a value of about 26 psi.

(c) From Boyle's law, we know that the product of pressure and volume (PV) for a given sample of gas at a constant temperature is always equal to the same value.

Therefore we have $P_1V_1 = k$ and $P_2V_2 = k$ which means that $P_1V_1 = P_2V_2$.

Using P_1 and V_1 as the known values 13.0 psi and 15.0 mL, P_2 as the pressure at which the volume is unknown, and V_2 as the unknown volume, we have:

Equation:

$$P_1V_1 = P_2V_2 \text{ or } 13.0 \text{ psi} \times 15.0 \text{ mL} = P_2 \times 7.5 \text{ mL}$$

Solving:

Equation:

$$P_2 = \frac{13.0 \text{ psi} \times 15.0 \text{ mL}}{7.5 \text{ mL}} = 26 \text{ psi}$$

It was more difficult to estimate well from the P - V graph, so (a) is likely more inaccurate than (b) or (c). The calculation will be as accurate as the equation and measurements allow.

Check Your Learning

The sample of gas in [\[link\]](#) has a volume of 30.0 mL at a pressure of 6.5 psi.

Determine the volume of the gas at a pressure of 11.0 psi, using:

(a) the P - V graph in [\[link\]](#)

(b) the $\frac{1}{P}$ vs. V graph in [\[link\]](#)

(c) the Boyle's law equation

Comment on the likely accuracy of each method.

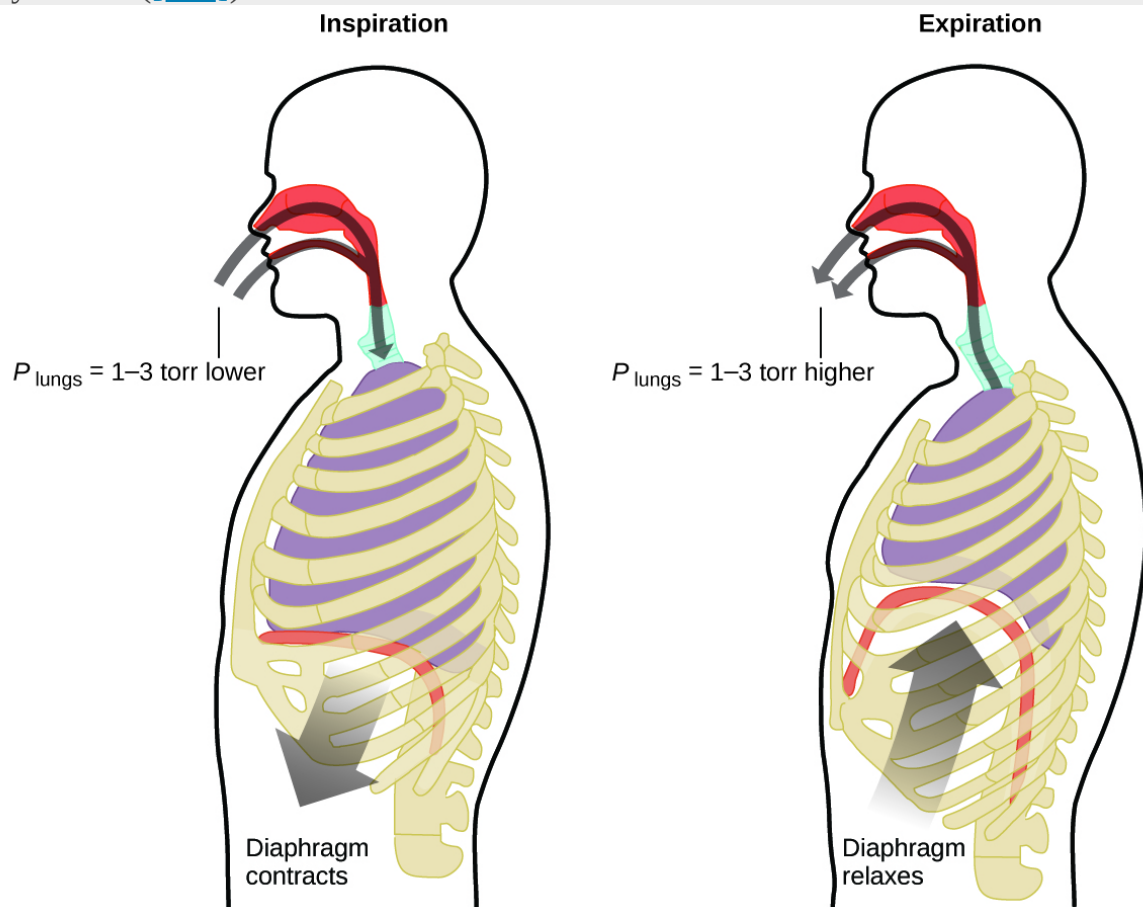
Note:

Answer:

(a) about 17–18 mL; (b) ~18 mL; (c) 17.7 mL; it was more difficult to estimate well from the P - V graph, so (a) is likely more inaccurate than (b); the calculation will be as accurate as the equation and measurements allow

Note:**Breathing and Boyle's Law**

What do you do about 20 times per minute for your whole life, without break, and often without even being aware of it? The answer, of course, is respiration, or breathing. How does it work? It turns out that the gas laws apply here. Your lungs take in gas that your body needs (oxygen) and get rid of waste gas (carbon dioxide). Lungs are made of spongy, stretchy tissue that expands and contracts while you breathe. When you inhale, your diaphragm and intercostal muscles (the muscles between your ribs) contract, expanding your chest cavity and making your lung volume larger. The increase in volume leads to a decrease in pressure (Boyle's law). This causes air to flow into the lungs (from high pressure to low pressure). When you exhale, the process reverses: Your diaphragm and rib muscles relax, your chest cavity contracts, and your lung volume decreases, causing the pressure to increase (Boyle's law again), and air flows out of the lungs (from high pressure to low pressure). You then breathe in and out again, and again, repeating this Boyle's law cycle for the rest of your life ([\[link\]](#)).



Breathing occurs because expanding and contracting lung volume creates small pressure differences between your lungs and your surroundings, causing air to be

drawn into and forced out of your lungs.

Moles of Gas and Volume: Avogadro's Law

The Italian scientist Amedeo Avogadro advanced a hypothesis in 1811 to account for the behavior of gases, stating that equal volumes of all gases, measured under the same conditions of temperature and pressure, contain the same number of molecules. Over time, this relationship was supported by many experimental observations as expressed by **Avogadro's law**: *For a confined gas, the volume (V) and number of moles (n) are directly proportional if the pressure and temperature both remain constant.*

In equation form, this is written as:

Equation:

$$V \propto n \quad \text{or} \quad V = k \times n \quad \text{or} \quad \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Mathematical relationships can also be determined for the other variable pairs, such as *P* versus *n*, and *n* versus *T*.

Note:



Visit this [interactive PhET simulation](#) to investigate the relationships between pressure, volume, temperature, and amount of gas. Use the simulation to examine the effect of changing one parameter on another while holding the other parameters constant (as described in the preceding sections on the various gas laws).

The Ideal Gas Law

To this point, four separate laws have been discussed that relate pressure, volume, temperature, and the number of moles of the gas:

- Boyle's law: $PV = \text{constant}$ at constant T and n
- Amontons's law: $\frac{P}{T} = \text{constant}$ at constant V and n
- Charles's law: $\frac{V}{T} = \text{constant}$ at constant P and n
- Avogadro's law: $\frac{V}{n} = \text{constant}$ at constant P and T

Combining these four laws yields the **ideal gas law**, a relation between the pressure, volume, temperature, and number of moles of a gas:

Equation:

$$PV = nRT$$

where P is the pressure of a gas, V is its volume, n is the number of moles of the gas, T is its temperature on the kelvin scale, and R is a constant called the **ideal gas constant** or the universal gas constant. The units used to express pressure, volume, and temperature will determine the proper form of the gas constant as required by dimensional analysis, the most commonly encountered values being $0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$ and $8.314 \text{ kPa L mol}^{-1} \text{ K}^{-1}$.

Gases whose properties of P , V , and T are accurately described by the ideal gas law (or the other gas laws) are said to exhibit *ideal behavior* or to approximate the traits of an **ideal gas**. An ideal gas is a hypothetical construct that may be used along with *kinetic molecular theory* to effectively explain the gas laws as will be described in a later module of this chapter. Although all the calculations presented in this module assume ideal behavior, this assumption is only reasonable for gases under conditions of relatively low pressure and high temperature. In the final module of this chapter, a modified gas law will be introduced that accounts for the *non-ideal* behavior observed for many gases at relatively high pressures and low temperatures.

The ideal gas equation contains five terms, the gas constant R and the variable properties P , V , n , and T . Specifying any four of these terms will permit use of the ideal gas law to calculate the fifth term as demonstrated in the following example exercises.

Example:

Using the Ideal Gas Law

Methane, CH_4 , is being considered for use as an alternative automotive fuel to replace gasoline. One gallon of gasoline could be replaced by 655 g of CH_4 . What is the

volume of this much methane at 25 °C and 745 torr?

Solution

We must rearrange $PV = nRT$ to solve for V : $V = \frac{nRT}{P}$

If we choose to use $R = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$, then the amount must be in moles, temperature must be in kelvin, and pressure must be in atm.

Converting into the “right” units:

Equation:

$$n = 655 \text{ g CH}_4 \times \frac{1 \text{ mol}}{16.043 \text{ g CH}_4} = 40.8 \text{ mol}$$

Equation:

$$T = 25 \text{ }^\circ\text{C} + 273 = 298 \text{ K}$$

Equation:

$$P = 745 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.980 \text{ atm}$$

Equation:

$$V = \frac{nRT}{P} = \frac{(40.8 \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{0.980 \text{ atm}} = 1.02 \times 10^3 \text{ L}$$

It would require 1020 L (269 gal) of gaseous methane at about 1 atm of pressure to replace 1 gal of gasoline. It requires a large container to hold enough methane at 1 atm to replace several gallons of gasoline.

Check Your Learning

Calculate the pressure in bar of 2520 moles of hydrogen gas stored at 27 °C in the 180-L storage tank of a modern hydrogen-powered car.

Note:

Answer:

350 bar

If the number of moles of an ideal gas are kept constant under two different sets of conditions, a useful mathematical relationship called the combined gas law is obtained: $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ using units of atm, L, and K. Both sets of conditions are equal to the product of $n \times R$ (where n = the number of moles of the gas and R is the ideal gas law constant).

Example:

Using the Combined Gas Law

When filled with air, a typical scuba tank with a volume of 13.2 L has a pressure of 153 atm ([\[link\]](#)). If the water temperature is 27 °C, how many liters of air will such a tank provide to a diver's lungs at a depth of approximately 70 feet in the ocean where the pressure is 3.13 atm?



Scuba divers use compressed air to breathe while underwater. (credit: modification of work by Mark Goodchild)

Letting 1 represent the air in the scuba tank and 2 represent the air in the lungs, and noting that body temperature (the temperature the air will be in the lungs) is 37 °C,

we have:

Equation:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \longrightarrow \frac{(153 \text{ atm}) (13.2 \text{ L})}{(300 \text{ K})} = \frac{(3.13 \text{ atm}) (V_2)}{(310 \text{ K})}$$

Solving for V_2 :

Equation:

$$V_2 = \frac{(153 \text{ atm}) (13.2 \text{ L}) (310 \text{ K})}{(300 \text{ K}) (3.13 \text{ atm})} = 667 \text{ L}$$

(Note: Be advised that this particular example is one in which the assumption of ideal gas behavior is not very reasonable, since it involves gases at relatively high pressures and low temperatures. Despite this limitation, the calculated volume can be viewed as a good “ballpark” estimate.)

Check Your Learning

A sample of ammonia is found to occupy 0.250 L under laboratory conditions of 27 °C and 0.850 atm. Find the volume of this sample at 0 °C and 1.00 atm.

Note:

Answer:

0.193 L

Note:

The Interdependence between Ocean Depth and Pressure in Scuba Diving

Whether scuba diving at the Great Barrier Reef in Australia (shown in [\[link\]](#)) or in the Caribbean, divers must understand how pressure affects a number of issues related to their comfort and safety.



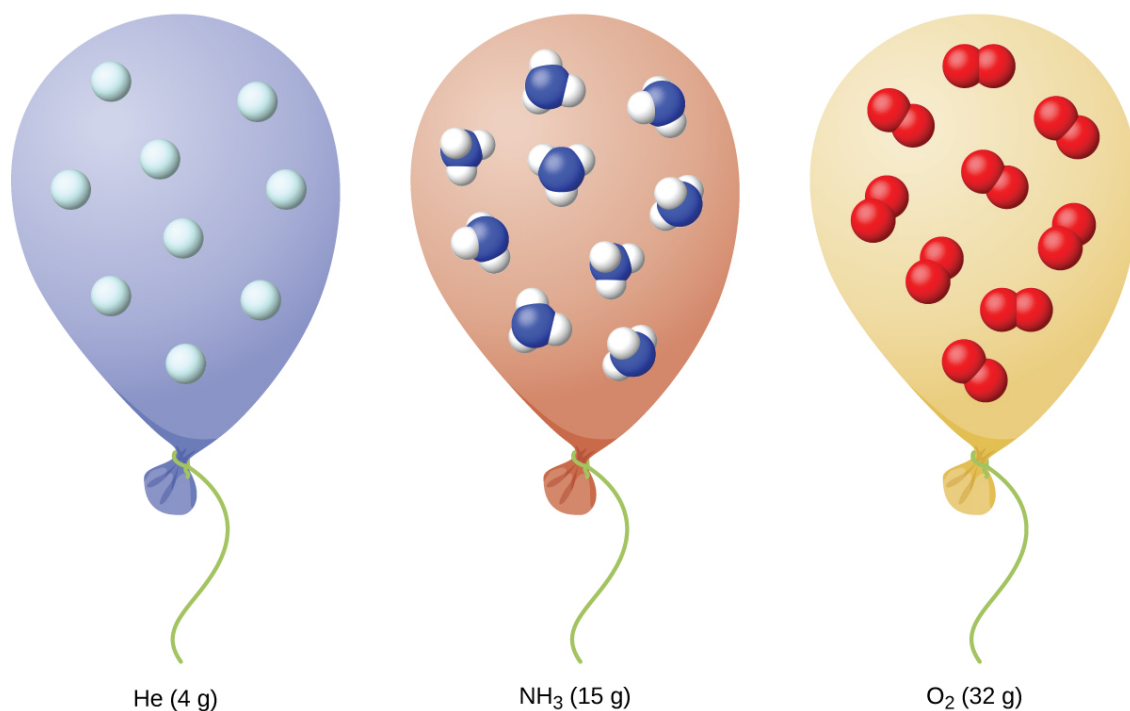
Scuba divers, whether at the Great Barrier Reef or in the Caribbean, must be aware of buoyancy, pressure equalization, and the amount of time they spend underwater, to avoid the risks associated with pressurized gases in the body. (credit: Kyle Taylor)

Pressure increases with ocean depth, and the pressure changes most rapidly as divers reach the surface. The pressure a diver experiences is the sum of all pressures above the diver (from the water and the air). Most pressure measurements are given in units of atmospheres, expressed as “atmospheres absolute” or ATA in the diving community: Every 33 feet of salt water represents 1 ATA of pressure in addition to 1 ATA of pressure from the atmosphere at sea level. As a diver descends, the increase in pressure causes the body’s air pockets in the ears and lungs to compress; on the ascent, the decrease in pressure causes these air pockets to expand, potentially rupturing eardrums or bursting the lungs. Divers must therefore undergo equalization by adding air to body airspaces on the descent by breathing normally and adding air to the mask by breathing out of the nose or adding air to the ears and sinuses by equalization techniques; the corollary is also true on ascent, divers must release air from the body to maintain equalization. Buoyancy, or the ability to control whether a diver sinks or floats, is controlled by the buoyancy compensator (BCD). If a diver is

ascending, the air in his BCD expands because of lower pressure according to Boyle's law (decreasing the pressure of gases increases the volume). The expanding air increases the buoyancy of the diver, and she or he begins to ascend. The diver must vent air from the BCD or risk an uncontrolled ascent that could rupture the lungs. In descending, the increased pressure causes the air in the BCD to compress and the diver sinks much more quickly; the diver must add air to the BCD or risk an uncontrolled descent, facing much higher pressures near the ocean floor. The pressure also impacts how long a diver can stay underwater before ascending. The deeper a diver dives, the more compressed the air that is breathed because of increased pressure: If a diver dives 33 feet, the pressure is 2 ATA and the air would be compressed to one-half of its original volume. The diver uses up available air twice as fast as at the surface.

Standard Conditions of Temperature and Pressure

We have seen that the volume of a given quantity of gas and the number of molecules (moles) in a given volume of gas vary with changes in pressure and temperature. Chemists sometimes make comparisons against a **standard temperature and pressure (STP)** for reporting properties of gases: 273.15 K and 1 atm (101.325 kPa). At STP, one mole of an ideal gas has a volume of about 22.4 L—this is referred to as the **standard molar volume** ([\[link\]](#)).



Since the number of moles in a given volume of gas varies with pressure and temperature changes, chemists use standard temperature and pressure (273.15 K and 1 atm or 101.325 kPa) to report properties of gases.

Key Concepts and Summary

The behavior of gases can be described by several laws based on experimental observations of their properties. The pressure of a given amount of gas is directly proportional to its absolute temperature, provided that the volume does not change (Amontons's law). The volume of a given gas sample is directly proportional to its absolute temperature at constant pressure (Charles's law). The volume of a given amount of gas is inversely proportional to its pressure when temperature is held constant (Boyle's law). Under the same conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules (Avogadro's law).

The equations describing these laws are special cases of the ideal gas law, $PV = nRT$, where P is the pressure of the gas, V is its volume, n is the number of moles of the gas, T is its kelvin temperature, and R is the ideal (universal) gas constant.

Key Equations

- $PV = nRT$

Chemistry End of Chapter Exercises

Exercise:

Problem:

Sometimes leaving a bicycle in the sun on a hot day will cause a blowout. Why?

Exercise:

Problem:

Explain how the volume of the bubbles exhausted by a scuba diver ([link](#)) change as they rise to the surface, assuming that they remain intact.

Solution:

As the bubbles rise, the pressure decreases, so their volume increases as suggested by Boyle's law.

Exercise:

Problem:

One way to state Boyle's law is "All other things being equal, the pressure of a gas is inversely proportional to its volume." (a) What is the meaning of the term "inversely proportional?" (b) What are the "other things" that must be equal?

Exercise:

Problem:

An alternate way to state Avogadro's law is "All other things being equal, the number of molecules in a gas is directly proportional to the volume of the gas." (a) What is the meaning of the term "directly proportional?" (b) What are the "other things" that must be equal?

Solution:

(a) The number of particles in the gas increases as the volume increases. (b) temperature, pressure

Exercise:

Problem:

How would the graph in [\[link\]](#) change if the number of moles of gas in the sample used to determine the curve were doubled?

Exercise:**Problem:**

How would the graph in [\[link\]](#) change if the number of moles of gas in the sample used to determine the curve were doubled?

Solution:

The curve would be farther to the right and higher up, but the same basic shape.

Exercise:**Problem:**

In addition to the data found in [\[link\]](#), what other information do we need to find the mass of the sample of air used to determine the graph?

Exercise:**Problem:**

Determine the volume of 1 mol of CH_4 gas at 150 K and 1 atm, using [\[link\]](#).

Solution:

About 12.2 L

Exercise:**Problem:**

Determine the pressure of the gas in the syringe shown in [\[link\]](#) when its volume is 12.5 mL, using:

(a) the appropriate graph

(b) Boyle's law

Exercise:

Problem:

A spray can is used until it is empty except for the propellant gas, which has a pressure of 1344 torr at 23 °C. If the can is thrown into a fire ($T = 475\text{ °C}$), what will be the pressure in the hot can?

Solution:

$$3.40 \times 10^3 \text{ torr}$$

Exercise:**Problem:**

What is the temperature of an 11.2-L sample of carbon monoxide, CO, at 744 torr if it occupies 13.3 L at 55 °C and 744 torr?

Exercise:**Problem:**

A 2.50-L volume of hydrogen measured at -196 °C is warmed to 100 °C . Calculate the volume of the gas at the higher temperature, assuming no change in pressure.

Solution:

$$12.1 \text{ L}$$

Exercise:**Problem:**

A balloon inflated with three breaths of air has a volume of 1.7 L. At the same temperature and pressure, what is the volume of the balloon if five more same-sized breaths are added to the balloon?

Exercise:**Problem:**

A weather balloon contains 8.80 moles of helium at a pressure of 0.992 atm and a temperature of 25 °C at ground level. What is the volume of the balloon under these conditions?



Solution:

217 L

Exercise:

Problem:

The volume of an automobile air bag was 66.8 L when inflated at 25 °C with 77.8 g of nitrogen gas. What was the pressure in the bag in kPa?

Exercise:

Problem:

How many moles of gaseous boron trifluoride, BF_3 , are contained in a 4.3410-L bulb at 788.0 K if the pressure is 1.220 atm? How many grams of BF_3 ?

Solution:

8.190×10^{-2} mol; 5.553 g

Exercise:

Problem:

Iodine, I_2 , is a solid at room temperature but sublimates (converts from a solid into a gas) when warmed. What is the temperature in a 73.3-mL bulb that contains 0.292 g of I_2 vapor at a pressure of 0.462 atm?

Exercise:

Problem: How many grams of gas are present in each of the following cases?

- (a) 0.100 L of CO_2 at 307 torr and 26°C
- (b) 8.75 L of C_2H_4 , at 378.3 kPa and 483 K
- (c) 221 mL of Ar at 0.23 torr and -54°C
-

Solution:

- (a) 7.24×10^{-2} g; (b) 23.1 g; (c) 1.5×10^{-4} g

Exercise:

Problem:

A high altitude balloon is filled with 1.41×10^4 L of hydrogen at a temperature of 21°C and a pressure of 745 torr. What is the volume of the balloon at a height of 20 km, where the temperature is -48°C and the pressure is 63.1 torr?

Exercise:

Problem:

A cylinder of medical oxygen has a volume of 35.4 L, and contains O_2 at a pressure of 151 atm and a temperature of 25°C . What volume of O_2 does this correspond to at normal body conditions, that is, 1 atm and 37°C ?

Solution:

5561 L

Exercise:

Problem:

A large scuba tank ([link](#)) with a volume of 18 L is rated for a pressure of 220 bar. The tank is filled at 20°C and contains enough air to supply 1860 L of air to a diver at a pressure of 2.37 atm (a depth of 45 feet). Was the tank filled to capacity at 20°C ?

Exercise:

Problem:

A 20.0-L cylinder containing 11.34 kg of butane, C_4H_{10} , was opened to the atmosphere. Calculate the mass of the gas remaining in the cylinder if it were opened and the gas escaped until the pressure in the cylinder was equal to the atmospheric pressure, 0.983 atm, and a temperature of 27°C .

Solution:

46.4 g

Exercise:**Problem:**

While resting, the average 70-kg human male consumes 14 L of pure O₂ per hour at 25 °C and 100 kPa. How many moles of O₂ are consumed by a 70 kg man while resting for 1.0 h?

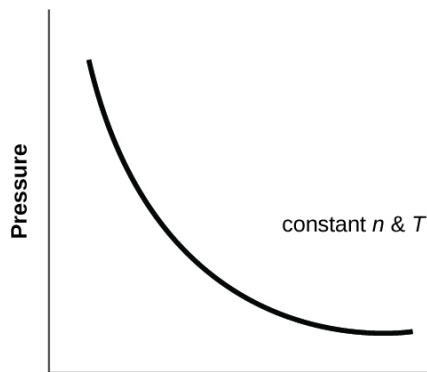
Exercise:**Problem:**

For a given amount of gas showing ideal behavior, draw labeled graphs of:

- (a) the variation of P with V
- (b) the variation of V with T
- (c) the variation of P with T
- (d) the variation of $\frac{1}{P}$ with V

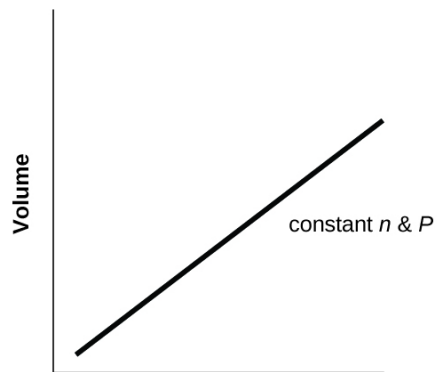
Solution:

For a gas exhibiting ideal behavior:



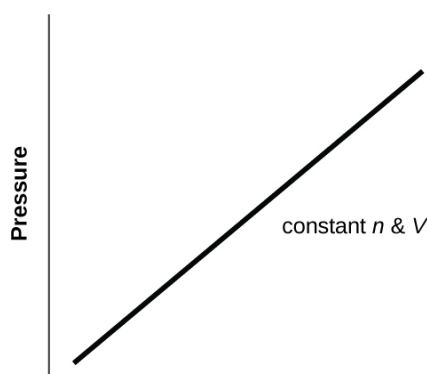
Volume

(a)



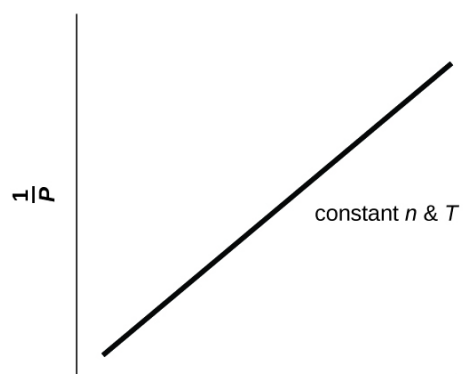
Temperature

(b)



Temperature

(c)



Volume

(d)

Exercise:

Problem:

A liter of methane gas, CH_4 , at STP contains more atoms of hydrogen than does a liter of pure hydrogen gas, H_2 , at STP. Using Avogadro's law as a starting point, explain why.

Exercise:

Problem:

The effect of chlorofluorocarbons (such as CCl_2F_2) on the depletion of the ozone layer is well known. The use of substitutes, such as $\text{CH}_3\text{CH}_2\text{F}(g)$, for the chlorofluorocarbons, has largely corrected the problem. Calculate the volume occupied by 10.0 g of each of these compounds at STP:

(a) $\text{CCl}_2\text{F}_2(g)$

(b) $\text{CH}_3\text{CH}_2\text{F}(g)$

Solution:

(a) 1.85 L CCl_2F_2 ; (b) 4.66 L $\text{CH}_3\text{CH}_2\text{F}$

Exercise:

Problem:

As 1 g of the radioactive element radium decays over 1 year, it produces 1.16×10^{18} alpha particles (helium nuclei). Each alpha particle becomes an atom of helium gas. What is the pressure in pascal of the helium gas produced if it occupies a volume of 125 mL at a temperature of 25 °C?

Exercise:

Problem:

A balloon that is 100.21 L at 21 °C and 0.981 atm is released and just barely clears the top of Mount Crumpet in British Columbia. If the final volume of the balloon is 144.53 L at a temperature of 5.24 °C, what is the pressure experienced by the balloon as it clears Mount Crumpet?

Solution:

0.644 atm

Exercise:

Problem:

If the temperature of a fixed amount of a gas is doubled at constant volume, what happens to the pressure?

Exercise:

Problem:

If the volume of a fixed amount of a gas is tripled at constant temperature, what happens to the pressure?

Solution:

The pressure decreases by a factor of 3.

Glossary

absolute zero

temperature at which the volume of a gas would be zero according to Charles's law.

Amontons's law

(also, Gay-Lussac's law) pressure of a given number of moles of gas is directly proportional to its kelvin temperature when the volume is held constant

Avogadro's law

volume of a gas at constant temperature and pressure is proportional to the number of gas molecules

Boyle's law

volume of a given number of moles of gas held at constant temperature is inversely proportional to the pressure under which it is measured

Charles's law

volume of a given number of moles of gas is directly proportional to its kelvin temperature when the pressure is held constant

ideal gas

hypothetical gas whose physical properties are perfectly described by the gas laws

ideal gas constant (R)

constant derived from the ideal gas equation $R = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$ or $8.314 \text{ L kPa mol}^{-1} \text{ K}^{-1}$

ideal gas law

relation between the pressure, volume, amount, and temperature of a gas under conditions derived by combination of the simple gas laws

standard conditions of temperature and pressure (STP)

273.15 K (0 °C) and 1 atm (101.325 kPa)

standard molar volume

volume of 1 mole of gas at STP, approximately 22.4 L for gases behaving ideally

Lewis Symbols and Structures

By the end of this section, you will be able to:

- Write Lewis symbols for neutral atoms and ions
- Draw Lewis structures depicting the bonding in simple molecules

Thus far in this chapter, we have discussed the various types of bonds that form between atoms and/or ions. In all cases, these bonds involve the sharing or transfer of valence shell electrons between atoms. In this section, we will explore the typical method for depicting valence shell electrons and chemical bonds, namely Lewis symbols and Lewis structures.

Lewis Symbols

We use Lewis symbols to describe valence electron configurations of atoms and monatomic ions. A **Lewis symbol** consists of an elemental symbol surrounded by one dot for each of its valence electrons:



[\[link\]](#) shows the Lewis symbols for the elements of the third period of the periodic table.

Atoms	Electronic Configuration	Lewis Symbol
sodium	$[\text{Ne}]3s^1$	$\text{Na}\cdot$
magnesium	$[\text{Ne}]3s^2$	$\cdot\text{Mg}\cdot$
aluminum	$[\text{Ne}]3s^23p^1$	$\cdot\overset{\cdot}{\underset{\cdot}{\text{Al}}}\cdot$
silicon	$[\text{Ne}]3s^23p^2$	$\cdot\overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{Si}}}}\cdot$
phosphorus	$[\text{Ne}]3s^23p^3$	$\cdot\overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{P}}}}}\cdot$
sulfur	$[\text{Ne}]3s^23p^4$	$:\overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{S}}}}}\cdot$
chlorine	$[\text{Ne}]3s^23p^5$	$:\overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{Cl}}}}}}\cdot$
argon	$[\text{Ne}]3s^23p^6$	$:\overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{Ar}}}}}}}:$

Lewis symbols illustrating the number of valence electrons for each element in the third period of the periodic table.

Lewis symbols can also be used to illustrate the formation of cations from atoms, as shown here for sodium and calcium:



Likewise, they can be used to show the formation of anions from atoms, as shown here for chlorine and sulfur:



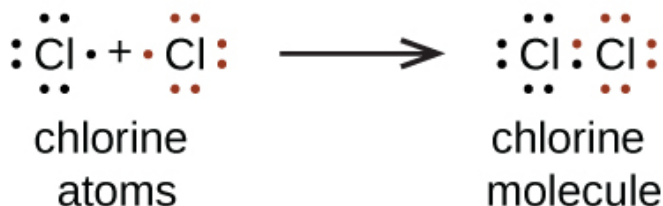
[\[link\]](#) demonstrates the use of Lewis symbols to show the transfer of electrons during the formation of ionic compounds.

Metal		Nonmetal		Ionic Compound
$\text{Na} \cdot$ sodium atom	+	$\cdot \ddot{\text{Cl}} \cdot$ chlorine atom	\longrightarrow	$\text{Na}^+ \left[\cdot \ddot{\text{Cl}} \cdot \right]^-$ sodium chloride (sodium ion and chloride ion)
$\cdot \text{Mg} \cdot$ magnesium atom	+	$\cdot \ddot{\text{O}} \cdot$ oxygen atom	\longrightarrow	$\text{Mg}^{2+} \left[\cdot \ddot{\text{O}} \cdot \right]^{2-}$ magnesium oxide (magnesium ion and oxide ion)
$\cdot \text{Ca} \cdot$ calcium atom	+	$2 \cdot \ddot{\text{F}} \cdot$ fluorine atoms	\longrightarrow	$\text{Ca}^{2+} \left[\cdot \ddot{\text{F}} \cdot \right]_2^-$ calcium fluoride (calcium ion and two fluoride ions)

Cations are formed when atoms lose electrons, represented by fewer Lewis dots, whereas anions are formed by atoms gaining electrons. The total number of electrons does not change.

Lewis Structures

We also use Lewis symbols to indicate the formation of covalent bonds, which are shown in **Lewis structures**, drawings that describe the bonding in molecules and polyatomic ions. For example, when two chlorine atoms form a chlorine molecule, they share one pair of electrons:



The Lewis structure indicates that each Cl atom has three pairs of electrons that are not used in bonding (called **lone pairs**) and one shared pair of electrons (written between the atoms). A dash (or line) is sometimes used to indicate a shared pair of electrons:



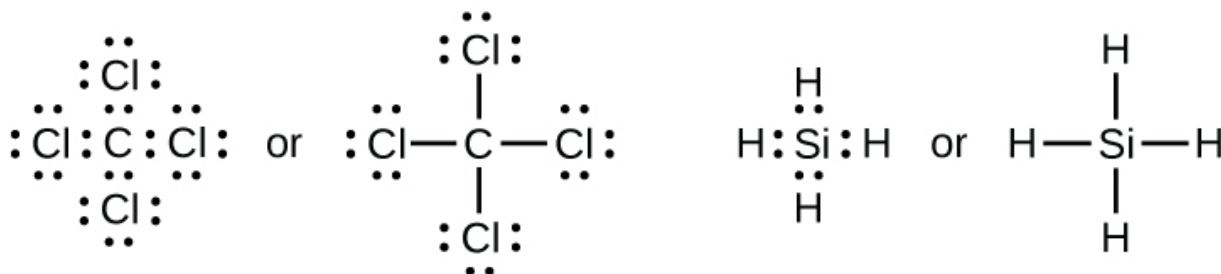
A single shared pair of electrons is called a **single bond**. Each Cl atom interacts with eight valence electrons: the six in the lone pairs and the two in the single bond.

The Octet Rule

The other halogen molecules (F_2 , Br_2 , I_2 , and At_2) form bonds like those in the chlorine molecule: one single bond between atoms and three lone pairs of electrons per atom. This allows each halogen atom to have a noble gas electron configuration. The tendency of main group atoms to form enough bonds to obtain eight valence electrons is known as the **octet rule**.

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F). For example, each atom of a group 14 element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming four covalent bonds, as illustrated here for carbon in CCl_4 (carbon tetrachloride) and silicon in SiH_4 (silane). Because hydrogen only needs two electrons

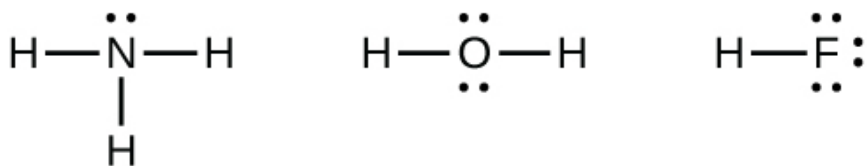
to fill its valence shell, it is an exception to the octet rule. The transition elements and inner transition elements also do not follow the octet rule:



carbon tetrachloride

silane

Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in NH_3 (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:



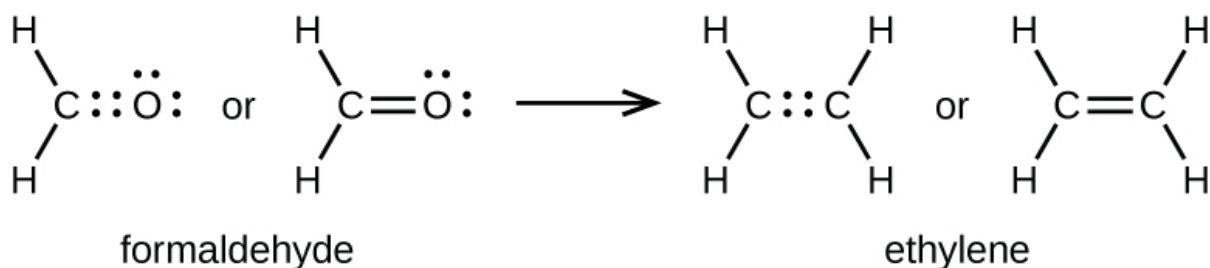
ammonia

Water

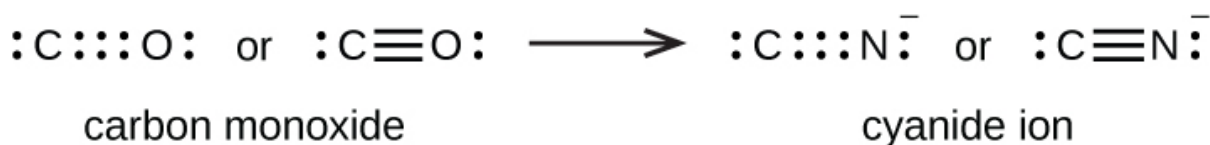
hydrogen
fluoride

Double and Triple Bonds

As previously mentioned, when a pair of atoms shares one pair of electrons, we call this a single bond. However, a pair of atoms may need to share more than one pair of electrons in order to achieve the requisite octet. A **double bond** forms when two pairs of electrons are shared between a pair of atoms, as between the carbon and oxygen atoms in CH_2O (formaldehyde) and between the two carbon atoms in C_2H_4 (ethylene):

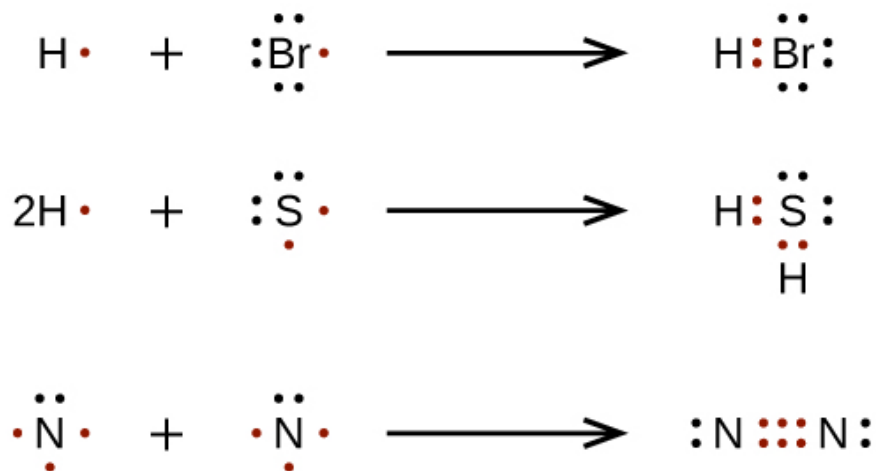


A **triple bond** forms when three electron pairs are shared by a pair of atoms, as in carbon monoxide (CO) and the cyanide ion (CN⁻):



Writing Lewis Structures with the Octet Rule

For very simple molecules and molecular ions, we can write the Lewis structures by merely pairing up the unpaired electrons on the constituent atoms. See these examples:



For more complicated molecules and molecular ions, it is helpful to follow the step-by-step procedure outlined here:

1. Determine the total number of valence (outer shell) electrons. For cations, subtract one electron for each positive charge. For anions, add one electron for each negative charge.
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom. (Generally, the least electronegative element should be placed in the

center.) Connect each atom to the central atom with a single bond (one electron pair).

3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.
4. Place all remaining electrons on the central atom.
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

Let us determine the Lewis structures of SiH_4 , CHO_2^- , NO^+ , and OF_2 as examples in following this procedure:

1. Determine the total number of valence (outer shell) electrons in the molecule or ion.

- For a molecule, we add the number of valence electrons on each atom in the molecule:

Equation:

$$\begin{array}{l} \text{SiH}_4 \\ \text{Si: } 4 \text{ valence electrons/atom} \times 1 \text{ atom} = 4 \\ + \text{ H: } 1 \text{ valence electron/atom} \times 4 \text{ atoms} = 4 \\ \hline \end{array} = 8 \text{ valence electrons}$$

- For a *negative ion*, such as CHO_2^- , we add the number of valence electrons on the atoms to the number of negative charges on the ion (one electron is gained for each single negative charge):

Equation:

$$\begin{array}{l} \text{CHO}_2^- \\ \text{C: } 4 \text{ valence electrons/atom} \times 1 \text{ atom} = 4 \\ \text{H: } 1 \text{ valence electron/atom} \times 1 \text{ atom} = 1 \\ \text{O: } 6 \text{ valence electrons/atom} \times 2 \text{ atoms} = 12 \\ + \quad \quad \quad 1 \text{ additional electron} = 1 \\ \hline \end{array} = 18 \text{ valence electrons}$$

- For a *positive ion*, such as NO^+ , we add the number of valence electrons on the atoms in the ion and then subtract the number of positive charges on the ion (one electron is lost for each single positive charge) from the total number of valence electrons:

Equation:



$$\text{N: } 5 \text{ valence electrons/atom} \times 1 \text{ atom} = 5$$

$$\text{O: } 6 \text{ valence electron/atom} \times 1 \text{ atom} = 6$$

$$+ \text{ } -1 \text{ electron (positive charge)} \quad = -1$$

$$= 10 \text{ valence electrons}$$

- Since OF_2 is a neutral molecule, we simply add the number of valence electrons:

Equation:

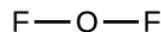
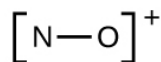
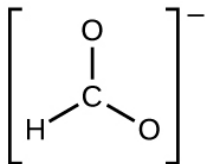
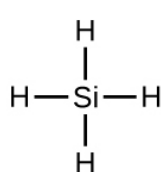


$$\text{O: } 6 \text{ valence electrons/atom} \times 1 \text{ atom} = 6$$

$$+ \text{ F: } 7 \text{ valence electrons/atom} \times 2 \text{ atoms} = 14$$

$$= 20 \text{ valence electrons}$$

2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. (Note that we denote ions with brackets around the structure, indicating the charge outside the brackets:)

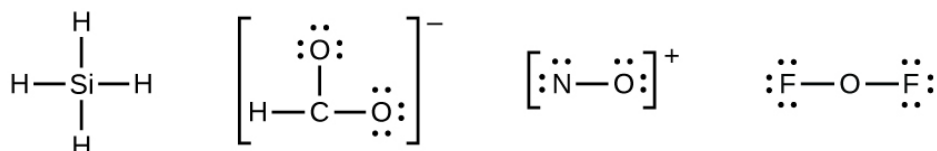


When several arrangements of atoms are possible, as for CHO_2^- , we must use experimental evidence to choose the correct one. In general, the less electronegative elements are more likely to be central atoms. In CHO_2^- , the less

electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it. Other examples include P in POCl_3 , S in SO_2 , and Cl in ClO_4^- . An exception is that hydrogen is almost never a central atom. As the most electronegative element, fluorine also cannot be a central atom.

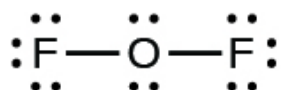
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.

- There are no remaining electrons on SiH_4 , so it is unchanged:



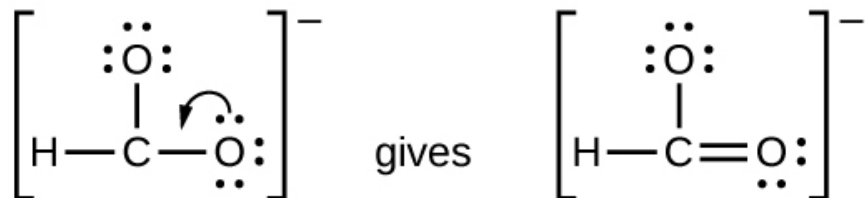
4. Place all remaining electrons on the central atom.

- For SiH_4 , CHO_2^- , and NO^+ , there are no remaining electrons; we already placed all of the electrons determined in Step 1.
- For OF_2 , we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central atom:

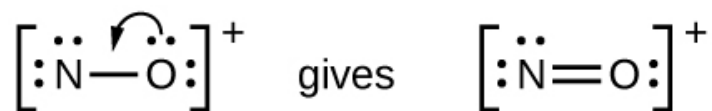


5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

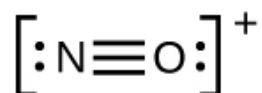
- SiH_4 : Si already has an octet, so nothing needs to be done.
- CHO_2^- : We have distributed the valence electrons as lone pairs on the oxygen atoms, but the carbon atom lacks an octet:



- NO^+ : For this ion, we added eight valence electrons, but neither atom has an octet. We cannot add any more electrons since we have already used the total that we found in Step 1, so we must move electrons to form a multiple bond:



This still does not produce an octet, so we must move another pair, forming a triple bond:



- In OF_2 , each atom has an octet as drawn, so nothing changes.

Example:

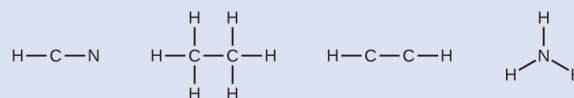
Writing Lewis Structures

NASA's Cassini-Huygens mission detected a large cloud of toxic hydrogen cyanide (HCN) on Titan, one of Saturn's moons. Titan also contains ethane (H_3CCH_3), acetylene (HCCH), and ammonia (NH_3). What are the Lewis structures of these molecules?

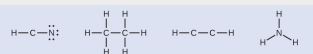
Solution

Calculate the number of valence electrons.
 $\text{HCN: } (1 \times 1) + (1 \times 1) + (5 \times 1) = 7$
 $\text{H}_3\text{CCH}_3: (1 \times 3) + (4 \times 2) + (1 \times 3) = 14$
 $\text{HCCH: } (1 \times 1) + (4 \times 2) + (1 \times 1) = 10$
 $\text{NH}_3: (1 \times 1) + (5 \times 3) = 8$

Draw a skeleton and connect the atoms with single bonds. Remember that H is never a central atom:

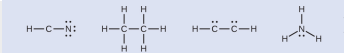
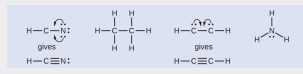


Where needed, distribute electrons to the terminal atoms:
Where



HCN: six electrons placed on N
 H_3CCH_3 : no electron remain
 HCCH : no terminal atoms capable of accepting electrons
 NH_3 : no terminal atoms capable of accepting electrons

HCN: H_3CCH_3 : no HCCH : NH_3 : two

needed, place remaining electrons on the central atom:		no electrons remain	electrons remain	four electrons placed on carbon	electrons placed on nitrogen
Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each atom:	HCN: H ₃ CCH ₃ : all form two more C–N bonds	all atoms have the correct number of electrons	HCCH: form a triple bond between the two carbon atoms	NH ₃ : all atoms have the correct number of electrons	

Check Your Learning

Both carbon monoxide, CO, and carbon dioxide, CO₂, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and CO₂ has been implicated in global climate change. What are the Lewis structures of these two molecules?

Note:

Answer:

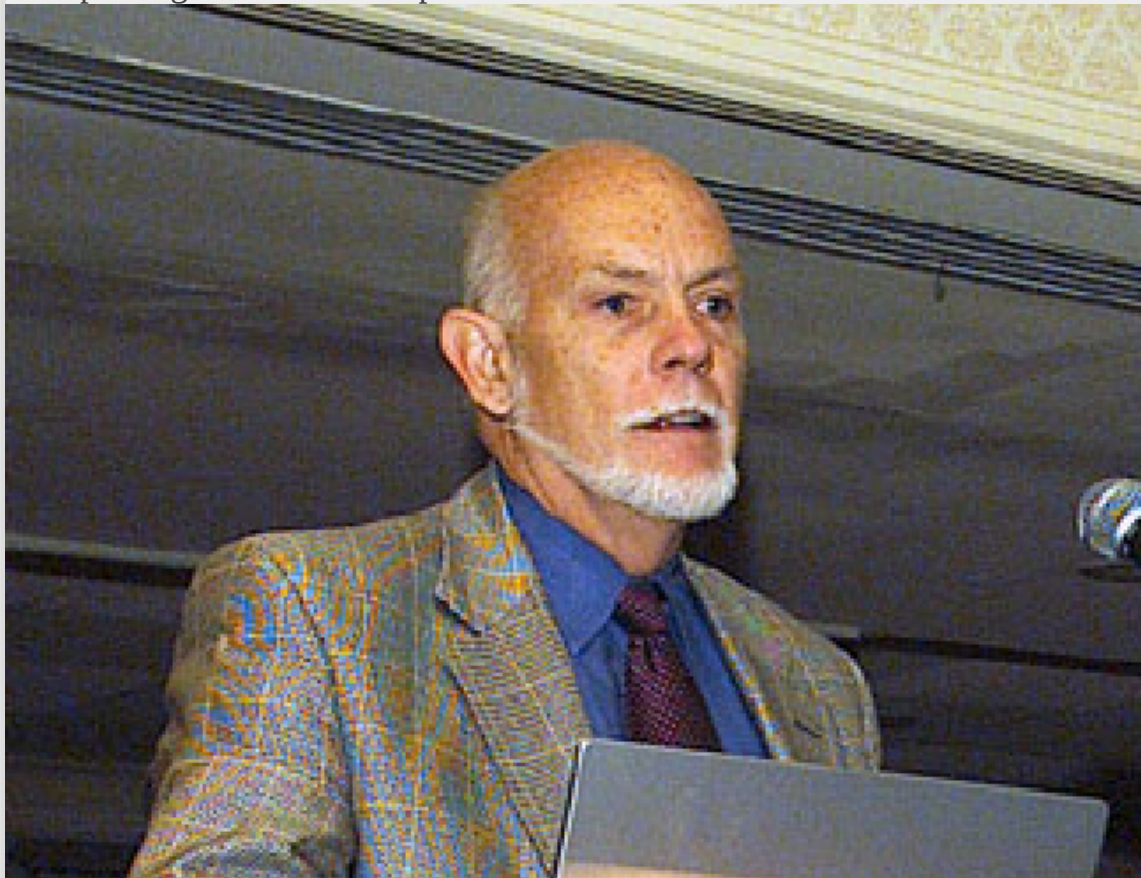


Note:

Fullerene Chemistry

Carbon soot has been known to man since prehistoric times, but it was not until fairly recently that the molecular structure of the main component of soot was discovered. In 1996, the Nobel Prize in Chemistry was awarded to Richard Smalley ([link](#)), Robert Curl, and Harold Kroto for their work in discovering a new form of carbon, the C₆₀ buckminsterfullerene molecule ([link](#)). An entire class of compounds, including spheres and tubes of various shapes, were discovered based on C₆₀. This

type of molecule, called a fullerene, shows promise in a variety of applications. Because of their size and shape, fullerenes can encapsulate other molecules, so they have shown potential in various applications from hydrogen storage to targeted drug delivery systems. They also possess unique electronic and optical properties that have been put to good use in solar powered devices and chemical sensors.



Richard Smalley (1943–2005), a professor of physics, chemistry, and astronomy at Rice University, was one of the leading advocates for fullerene chemistry. Upon his death in 2005, the US Senate honored him as the “Father of Nanotechnology.” (credit: United States Department of Energy)

Exceptions to the Octet Rule

Many covalent molecules have central atoms that do not have eight electrons in their Lewis structures. These molecules fall into three categories:

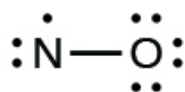
- Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired electron.
- Electron-deficient molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Hypervalent molecules have a central atom that has more electrons than needed for a noble gas configuration.

Odd-electron Molecules

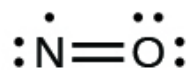
We call molecules that contain an odd number of electrons **free radicals**. Nitric oxide, NO, is an example of an odd-electron molecule; it is produced in internal combustion engines when oxygen and nitrogen react at high temperatures.

To draw the Lewis structure for an odd-electron molecule like NO, we follow the same five steps we would for other molecules, but with a few minor changes:

1. *Determine the total number of valence (outer shell) electrons.* The sum of the valence electrons is 5 (from N) + 6 (from O) = 11. The odd number immediately tells us that we have a free radical, so we know that not every atom can have eight electrons in its valence shell.
2. *Draw a skeleton structure of the molecule.* We can easily draw a skeleton with an N–O single bond:
N–O
3. *Distribute the remaining electrons as lone pairs on the terminal atoms.* In this case, there is no central atom, so we distribute the electrons around both atoms. We give eight electrons to the more electronegative atom in these situations; thus oxygen has the filled valence shell:

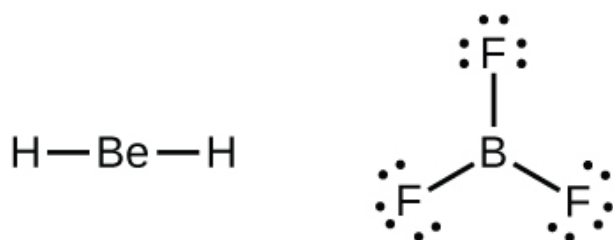


4. *Place all remaining electrons on the central atom.* Since there are no remaining electrons, this step does not apply.
5. *Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible.* We know that an odd-electron molecule cannot have an octet for every atom, but we want to get each atom as close to an octet as possible. In this case, nitrogen has only five electrons around it. To move closer to an octet for nitrogen, we take one of the lone pairs from oxygen and use it to form a NO double bond. (We cannot take another lone pair of electrons on oxygen and form a triple bond because nitrogen would then have nine electrons:)

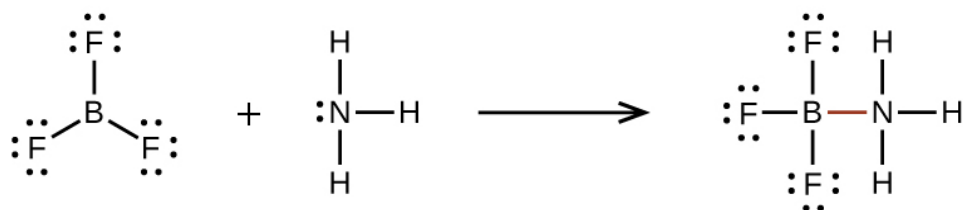


Electron-deficient Molecules

We will also encounter a few molecules that contain central atoms that do not have a filled valence shell. Generally, these are molecules with central atoms from groups 2 and 13, outer atoms that are hydrogen, or other atoms that do not form multiple bonds. For example, in the Lewis structures of beryllium dihydride, BeH_2 , and boron trifluoride, BF_3 , the beryllium and boron atoms each have only four and six electrons, respectively. It is possible to draw a structure with a double bond between a boron atom and a fluorine atom in BF_3 , satisfying the octet rule, but experimental evidence indicates the bond lengths are closer to that expected for B–F single bonds. This suggests the best Lewis structure has three B–F single bonds and an electron deficient boron. The reactivity of the compound is also consistent with an electron deficient boron. However, the B–F bonds are slightly shorter than what is actually expected for B–F single bonds, indicating that some double bond character is found in the actual molecule.

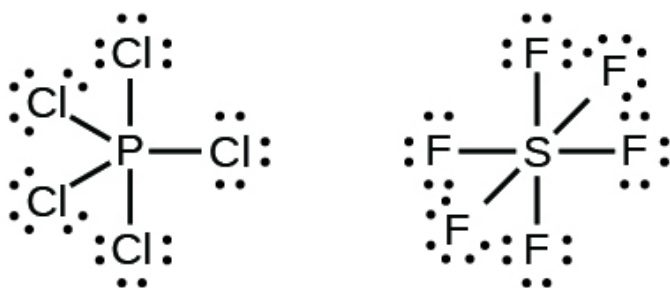


An atom like the boron atom in BF_3 , which does not have eight electrons, is very reactive. It readily combines with a molecule containing an atom with a lone pair of electrons. For example, NH_3 reacts with BF_3 because the lone pair on nitrogen can be shared with the boron atom:



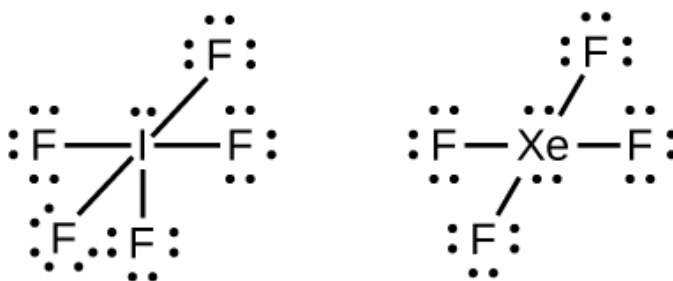
Hypervalent Molecules

Elements in the second period of the periodic table ($n = 2$) can accommodate only eight electrons in their valence shell orbitals because they have only four valence orbitals (one $2s$ and three $2p$ orbitals). Elements in the third and higher periods ($n \geq 3$) have more than four valence orbitals and can share more than four pairs of electrons with other atoms because they have empty d orbitals in the same shell. Molecules formed from these elements are sometimes called **hypervalent molecules**. [\[link\]](#) shows the Lewis structures for two hypervalent molecules, PCl_5 and SF_6 .



In PCl_5 , the central atom phosphorus shares five pairs of electrons. In SF_6 , sulfur shares six pairs of electrons.

In some hypervalent molecules, such as IF_5 and XeF_4 , some of the electrons in the outer shell of the central atom are lone pairs:



When we write the Lewis structures for these molecules, we find that we have electrons left over after filling the valence shells of the outer atoms with eight electrons. These additional electrons must be assigned to the central atom.

Example:

Writing Lewis Structures: Octet Rule Violations

Xenon is a noble gas, but it forms a number of stable compounds. We examined XeF_4 earlier. What are the Lewis structures of XeF_2 and XeF_6 ?

Solution

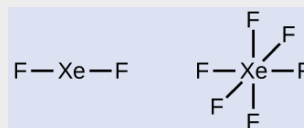
We can draw the Lewis structure of any covalent molecule by following the six steps discussed earlier. In this case, we can condense the last few steps, since not all of them apply.

Calculate the number of valence electrons:

$$\begin{array}{l} \text{XeF}_2: 8 + 2 \times 7 = 22 \\ \text{XeF}_6: 8 + 6 \times 7 = 50 \end{array}$$

Draw a skeleton joining the atoms by single bonds.

Xenon will be the central atom because fluorine cannot be a central atom:



Distribute the remaining electrons.

XeF_2 : We place three lone pairs of electrons around each F atom, accounting for 12 electrons and giving each F atom 8 electrons. Thus, six electrons (three lone pairs) remain. These lone pairs must be placed on the Xe atom. This is acceptable because Xe atoms have empty valence shell

d orbitals and 2s orbitals can accommodate more than eight electrons. The Lewis structure of XeF_6 shows two bonding pairs and three lone pairs of electrons around the Xe atom:

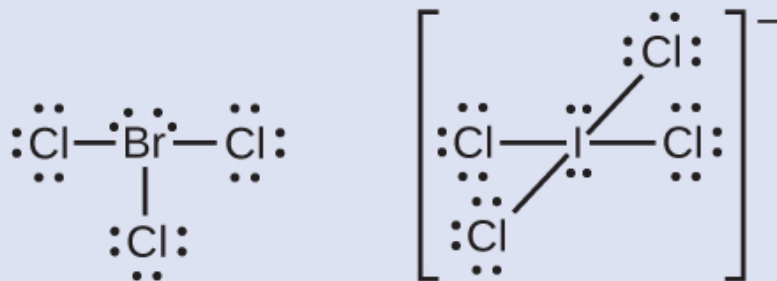
XeF_6 : We place three lone pairs of electrons around each F atom, accounting for 36 electrons. Two electrons remain, and this lone pair is placed on the Xe atom:

Check Your Learning

The halogens form a class of compounds called the interhalogens, in which halogen atoms covalently bond to each other. Write the Lewis structures for the interhalogens BrCl_3 and ICl_4^- .

Note:

Answer:



Key Concepts and Summary

Valence electronic structures can be visualized by drawing Lewis symbols (for atoms and monatomic ions) and Lewis structures (for molecules and polyatomic ions). Lone pairs, unpaired electrons, and single, double, or triple bonds are used to indicate where the valence electrons are located around each atom in a Lewis structure. Most structures—especially those containing second row elements—obey the octet rule, in which every atom (except H) is surrounded by eight electrons. Exceptions to the octet rule occur for odd-electron molecules (free radicals), electron-deficient molecules, and hypervalent molecules.

Chemistry End of Chapter Exercises

Exercise:

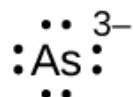
Problem: Write the Lewis symbols for each of the following ions:



(g) N^{3-}

Solution:

(a) eight electrons:



;

(b) eight electrons:

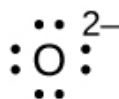


;

(c) no electrons

 $\text{Be}^{2+};$

(d) eight electrons:



;

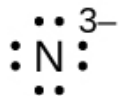
(e) no electrons

 Ga^{3+} ;

(f) no electrons

 Li^+ ;

(g) eight electrons:



Exercise:

Problem:

Many monatomic ions are found in seawater, including the ions formed from the following list of elements. Write the Lewis symbols for the monatomic ions formed from the following elements:

(a) Cl

(b) Na

(c) Mg

(d) Ca

(e) K

(f) Br

(g) Sr

(h) F

Exercise:

Problem:

Write the Lewis symbols of the ions in each of the following ionic compounds and the Lewis symbols of the atom from which they are formed:

(a) MgS

(b) Al₂O₃

(c) GaCl₃

(d) K₂O

(e) Li₃N

(f) KF

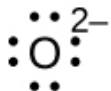
Solution:

(a)

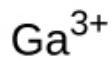


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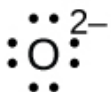
(b)



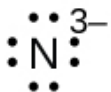
;
(c)



;
(d)



;
(e)



;
(f)

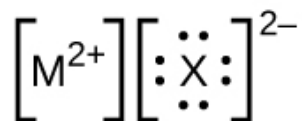


Exercise:

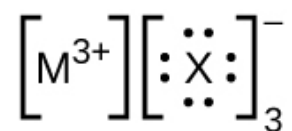
Problem:

In the Lewis structures listed here, M and X represent various elements in the third period of the periodic table. Write the formula of each compound using the chemical symbols of each element:

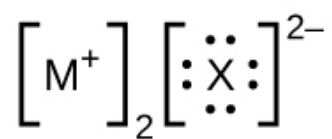
(a)



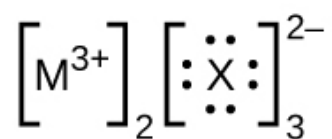
(b)



(c)



(d)



Exercise:

Problem:

Write the Lewis structure for the diatomic molecule P_2 , an unstable form of phosphorus found in high-temperature phosphorus vapor.

Solution:



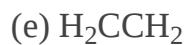
Exercise:

Problem: Write Lewis structures for the following:

(a) H_2

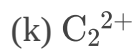
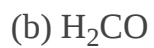
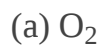
(b) HBr

(c) PCl_3



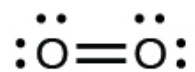
Exercise:

Problem: Write Lewis structures for the following:



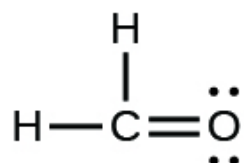
Solution:





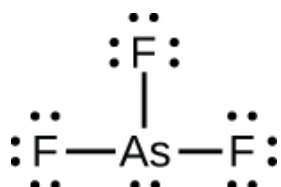
In this case, the Lewis structure is inadequate to depict the fact that experimental studies have shown two unpaired electrons in each oxygen molecule.

(b)



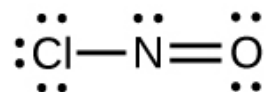
;

(c)



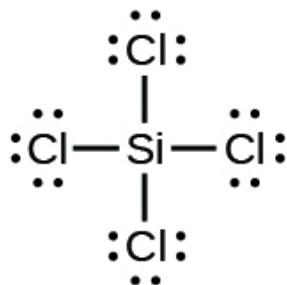
;

(d)



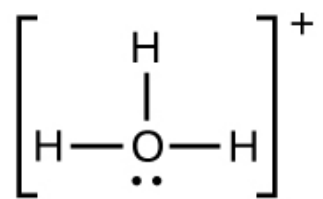
;

(e)

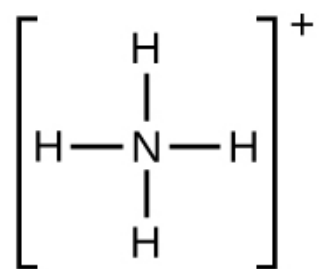


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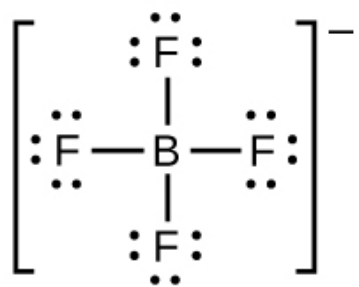
(f)



;
(g)



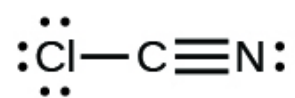
;
(h)



;
(i)



;
(j)



;
(k)



Exercise:

Problem: Write Lewis structures for the following:

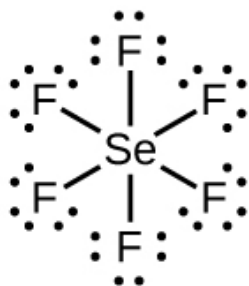


Exercise:

Problem: Write Lewis structures for the following:

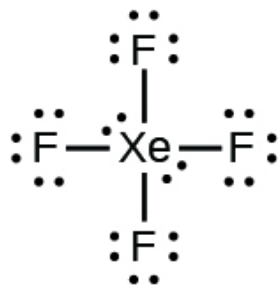


Solution:



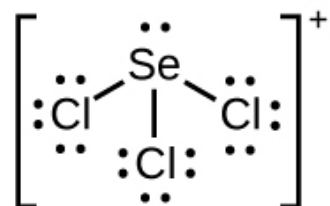
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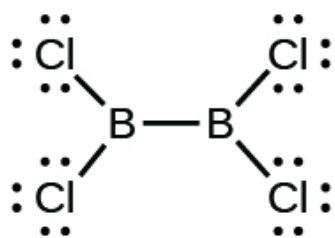
;

(c) SeCl_3^+ :



;

(d) Cl_2BBCl_2 :



Exercise:

Problem: Write Lewis structures for:

(a) PO_4^{3-}

(b) ICl_4^-

(c) SO_3^{2-}

(d) HONO

Exercise:

Problem:

Correct the following statement: “The bonds in solid PbCl_2 are ionic; the bond in a HCl molecule is covalent. Thus, all of the valence electrons in PbCl_2 are located on the Cl^- ions, and all of the valence electrons in a HCl molecule are shared between the H and Cl atoms.”

Solution:

Two valence electrons per Pb atom are transferred to Cl atoms; the resulting Pb^{2+} ion has a $6s^2$ valence shell configuration. Two of the valence electrons in the HCl molecule are shared, and the other six are located on the Cl atom as lone pairs of electrons.

Exercise:

Problem: Write Lewis structures for the following molecules or ions:

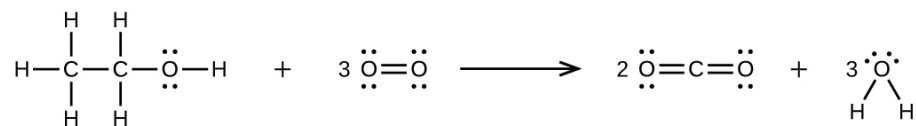
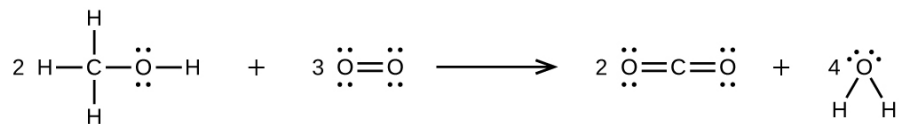
(a) SbH_3

(b) XeF_2

(c) Se_8 (a cyclic molecule with a ring of eight Se atoms)

Exercise:**Problem:**

Methanol, H_3COH , is used as the fuel in some race cars. Ethanol, $\text{C}_2\text{H}_5\text{OH}$, is used extensively as motor fuel in Brazil. Both methanol and ethanol produce CO_2 and H_2O when they burn. Write the chemical equations for these combustion reactions using Lewis structures instead of chemical formulas.

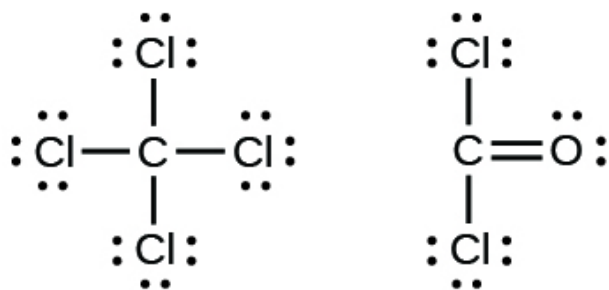
Solution:

Exercise:**Problem:**

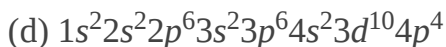
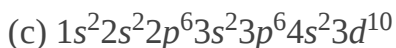
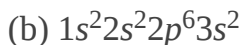
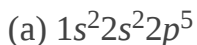
Many planets in our solar system contain organic chemicals including methane (CH_4) and traces of ethylene (C_2H_4), ethane (C_2H_6), propyne (H_3CCCH), and diacetylene (HCCCCCH). Write the Lewis structures for each of these molecules.

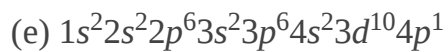
Exercise:**Problem:**

Carbon tetrachloride was formerly used in fire extinguishers for electrical fires. It is no longer used for this purpose because of the formation of the toxic gas phosgene, Cl_2CO . Write the Lewis structures for carbon tetrachloride and phosgene.

Solution:**Exercise:****Problem:**

Identify the atoms that correspond to each of the following electron configurations. Then, write the Lewis symbol for the common ion formed from each atom:



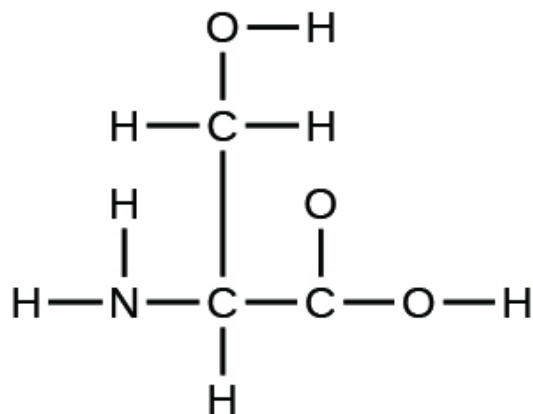


Exercise:

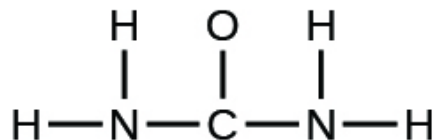
Problem:

The arrangement of atoms in several biologically important molecules is given here. Complete the Lewis structures of these molecules by adding multiple bonds and lone pairs. Do not add any more atoms.

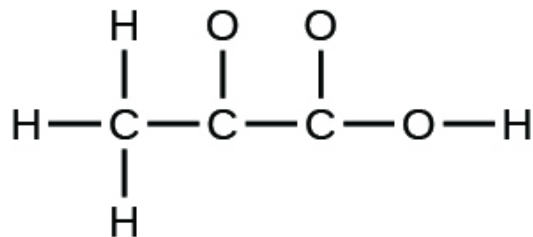
(a) the amino acid serine:



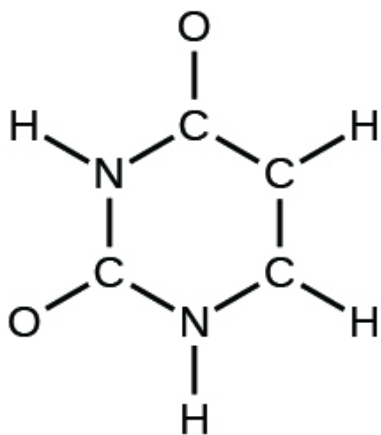
(b) urea:



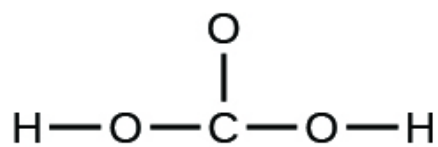
(c) pyruvic acid:



(d) uracil:

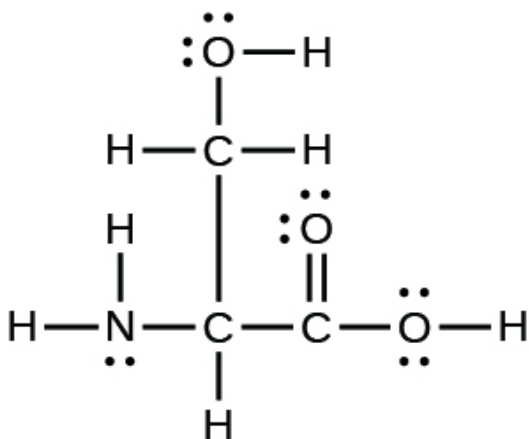


(e) carbonic acid:



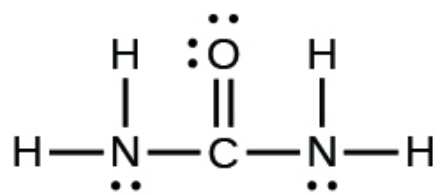
Solution:

(a)

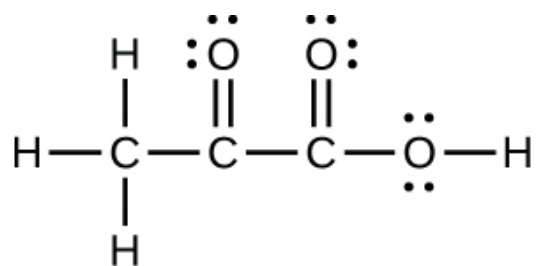


;

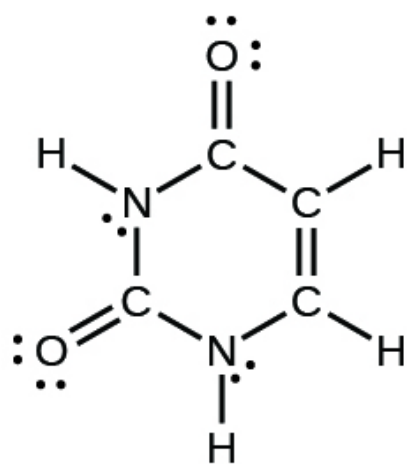
(b)



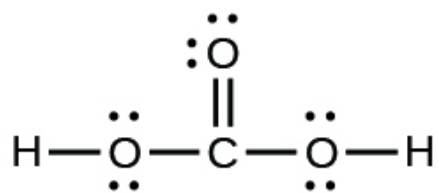
;
(c)



;
(d)



;
(e)



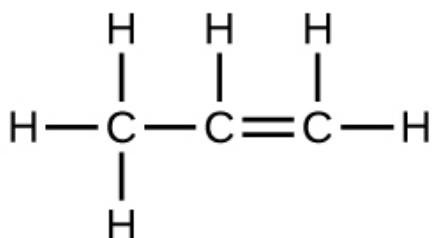
Exercise:

Problem:

A compound with a molar mass of about 28 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

Exercise:**Problem:**

A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

Solution:**Exercise:****Problem:**

Two arrangements of atoms are possible for a compound with a molar mass of about 45 g/mol that contains 52.2% C, 13.1% H, and 34.7% O by mass. Write the Lewis structures for the two molecules.

Exercise:

Problem: How are single, double, and triple bonds similar? How do they differ?

Solution:

Each bond includes a sharing of electrons between atoms. Two electrons are shared in a single bond; four electrons are shared in a double bond; and six electrons are shared in a triple bond.

Glossary

double bond

covalent bond in which two pairs of electrons are shared between two atoms

free radical

molecule that contains an odd number of electrons

hypervalent molecule

molecule containing at least one main group element that has more than eight electrons in its valence shell

Lewis structure

diagram showing lone pairs and bonding pairs of electrons in a molecule or an ion

Lewis symbol

symbol for an element or monatomic ion that uses a dot to represent each valence electron in the element or ion

lone pair

two (a pair of) valence electrons that are not used to form a covalent bond

octet rule

guideline that states main group atoms will form structures in which eight valence electrons interact with each nucleus, counting bonding electrons as interacting with both atoms connected by the bond

single bond

bond in which a single pair of electrons is shared between two atoms

triple bond

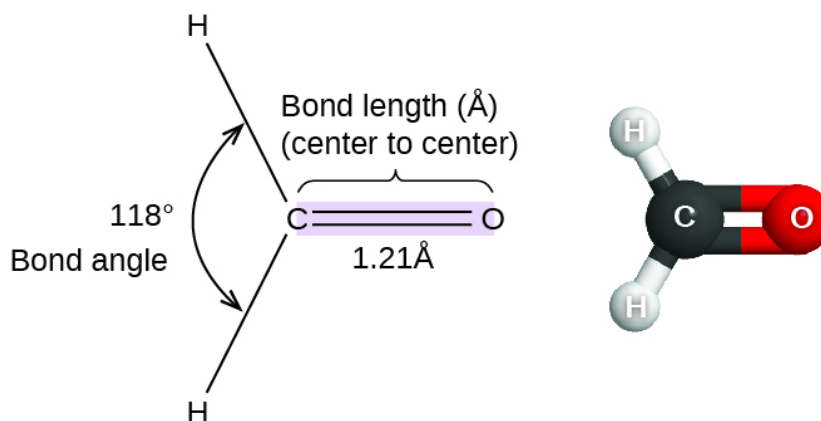
bond in which three pairs of electrons are shared between two atoms

Molecular Structure and Polarity

By the end of this section, you will be able to:

- Predict the structures of small molecules using valence shell electron pair repulsion (VSEPR) theory
- Explain the concepts of polar covalent bonds and molecular polarity
- Assess the polarity of a molecule based on its bonding and structure

Thus far, we have used two-dimensional Lewis structures to represent molecules. However, molecular structure is actually three-dimensional, and it is important to be able to describe molecular bonds in terms of their distances, angles, and relative arrangements in space ([\[link\]](#)). A **bond angle** is the angle between any two bonds that include a common atom, usually measured in degrees. A **bond distance** (or bond length) is the distance between the nuclei of two bonded atoms along the straight line joining the nuclei. Bond distances are measured in Ångstroms ($1 \text{ Å} = 10^{-10} \text{ m}$) or picometers ($1 \text{ pm} = 10^{-12} \text{ m}$, $100 \text{ pm} = 1 \text{ Å}$).



Bond distances (lengths) and angles are shown for the formaldehyde molecule, H₂CO.

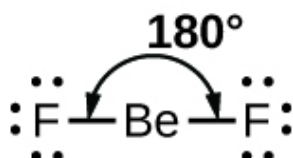
VSEPR Theory

Valence shell electron-pair repulsion theory (VSEPR theory) enables us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule from an examination of the number of bonds and lone electron pairs in its Lewis structure. The VSEPR model assumes that

electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them. The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs. The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.

VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct arrangement of atoms in a molecule. We should understand, however, that the theory only considers electron-pair repulsions. Other interactions, such as nuclear-nuclear repulsions and nuclear-electron attractions, are also involved in the final arrangement that atoms adopt in a particular molecular structure.

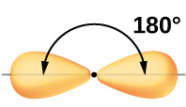
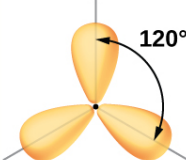
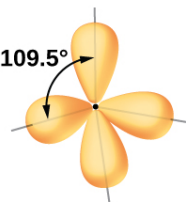
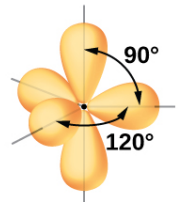
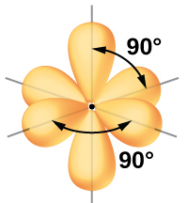
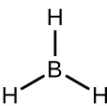
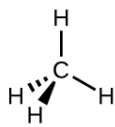


As a simple example of VSEPR theory, let us predict the structure of a gaseous BeF_2 molecule. The Lewis structure of BeF_2 ([\[link\]](#)) shows only two electron pairs around the central beryllium atom. With two bonds and no lone pairs of electrons on the central atom, the bonds are as far apart as possible, and the electrostatic repulsion between these regions of high electron density is reduced to a minimum when they are on opposite sides of the central atom. The bond angle is 180° ([\[link\]](#)).



The BeF_2 molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom.

[\[link\]](#) illustrates this and other electron-pair geometries that minimize the repulsions among regions of high electron density (bonds and/or lone pairs). Two regions of electron density around a central atom in a molecule form a

linear geometry; three regions form a **trigonal planar** geometry; four regions form a **tetrahedral** geometry; five regions form a **trigonal bipyramidal** geometry; and six regions form an **octahedral** geometry.

Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement					
Line-dash-wedge notation	$\text{H}-\text{Be}-\text{H}$				
Electron pair geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

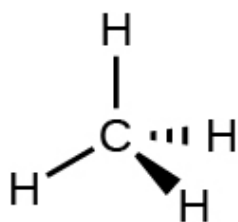
The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

Electron-pair Geometry versus Molecular Structure

It is important to note that electron-pair geometry around a central atom is *not* the same thing as its molecular structure. The electron-pair geometries shown in [\[link\]](#) describe all regions where electrons are located, bonds as well as lone pairs. Molecular structure describes the location of the *atoms*, not the electrons.

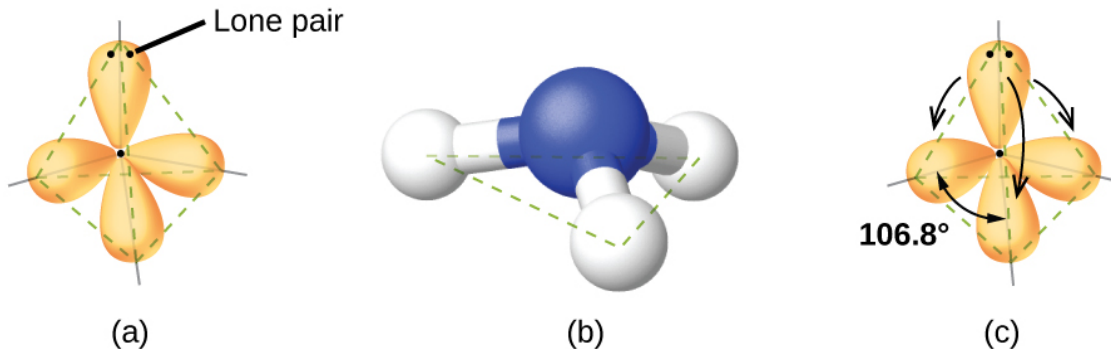
We differentiate between these two situations by naming the geometry that includes *all* electron pairs the **electron-pair geometry**. The structure that includes only the placement of the atoms in the molecule is called the **molecular structure**. The electron-pair geometries will be the same as the molecular structures when there are no lone electron pairs around the central atom, but they will be different when there are lone pairs present on the central atom.

For example, the methane molecule, CH_4 , which is the major component of natural gas, has four bonding pairs of electrons around the central carbon atom; the electron-pair geometry is tetrahedral, as is the molecular structure ([\[link\]](#)). On the other hand, the ammonia molecule, NH_3 , also has four electron pairs associated with the nitrogen atom, and thus has a tetrahedral electron-pair geometry. One of these regions, however, is a lone pair, which is not included in the molecular structure, and this lone pair influences the shape of the molecule ([\[link\]](#)).



The
molecular
structure of
the methane
molecule,
 CH_4 , is
shown with

a
tetrahedral
arrangement
of the
hydrogen
atoms.
VSEPR
structures
like this one
are often
drawn using
the wedge
and dash
notation, in
which solid
lines
represent
bonds in the
plane of the
page, solid
wedges
represent
bonds
coming up
out of the
plane, and
dashed lines
represent
bonds going
down into
the plane.



(a) The electron-pair geometry for the ammonia molecule is tetrahedral with one lone pair and three single bonds. (b) The trigonal pyramidal molecular structure is determined from the electron-pair geometry. (c) The actual bond angles deviate slightly from the idealized angles because the lone pair takes up a larger region of space than do the single bonds, causing the HNH angle to be slightly smaller than 109.5° .

As seen in [\[link\]](#), small distortions from the ideal angles in [\[link\]](#) can result from differences in repulsion between various regions of electron density. VSEPR theory predicts these distortions by establishing an order of repulsions and an order of the amount of space occupied by different kinds of electron pairs. The order of electron-pair repulsions from greatest to least repulsion is:

Equation:

lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair

This order of repulsions determines the amount of space occupied by different regions of electrons. A lone pair of electrons occupies a larger region of space than the electrons in a triple bond; in turn, electrons in a triple bond occupy more space than those in a double bond, and so on. The order of sizes from largest to smallest is:


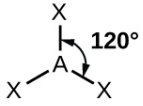
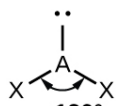
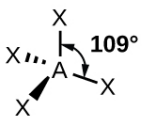


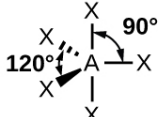
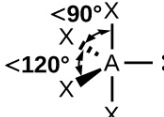
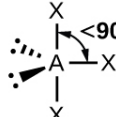
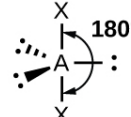
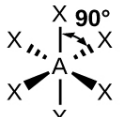
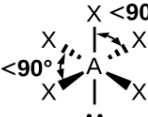
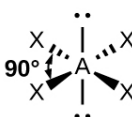


Equation:

lone pair > triple bond > double bond > single bond

Consider formaldehyde, H_2CO , which is used as a preservative for biological and anatomical specimens ([\[link\]](#)). This molecule has regions of high electron

density that consist of two single bonds and one double bond. The basic geometry is trigonal planar with 120° bond angles, but we see that the double bond causes slightly larger angles (121°), and the angle between the single bonds is slightly smaller (118°).

In the ammonia molecule, the three hydrogen atoms attached to the central nitrogen are not arranged in a flat, trigonal planar molecular structure, but rather in a three-dimensional trigonal pyramid ([\[link\]](#)) with the nitrogen atom at the apex and the three hydrogen atoms forming the base. The ideal bond angles in a trigonal pyramid are based on the tetrahedral electron pair geometry. Again, there are slight deviations from the ideal because lone pairs occupy larger regions of space than do bonding electrons. The H–N–H bond angles in NH_3 are slightly smaller than the 109.5° angle in a regular tetrahedron ([\[link\]](#)) because the lone pair-bonding pair repulsion is greater than the bonding pair-bonding pair repulsion ([\[link\]](#)). [\[link\]](#) illustrates the ideal molecular structures, which are predicted based on the electron-pair geometries for various combinations of lone pairs and bonding pairs.

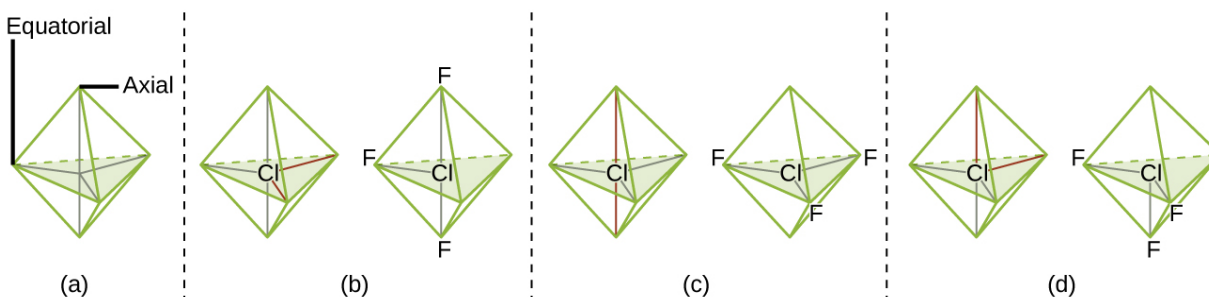
Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal planar	 Bent or angular			
4	 Tetrahedral	 Trigonal pyramid	 Bent or angular		
5	 Trigonal bipyramid	 Sawhorse or seesaw	 T-shape	 Linear	
6	 Octahedral	 Square pyramid	 Square planar	 T-shape	 Linear

The molecular structures are identical to the electron-pair geometries when there are no lone pairs present (first column). For a particular number of electron pairs (row), the molecular structures for one or more lone pairs are determined based on modifications of the corresponding electron-pair geometry.

According to VSEPR theory, the terminal atom locations (Xs in [\[link\]](#)) are equivalent within the linear, trigonal planar, and tetrahedral electron-pair geometries (the first three rows of the table). It does not matter which X is replaced with a lone pair because the molecules can be rotated to convert positions. For trigonal bipyramidal electron-pair geometries, however, there are two distinct X positions, as shown in [\[link\]](#): an **axial position** (if we hold a model of a trigonal bipyramid by the two axial positions, we have an axis

around which we can rotate the model) and an **equatorial position** (three positions form an equator around the middle of the molecule). As shown in [\[link\]](#), the axial position is surrounded by bond angles of 90° , whereas the equatorial position has more space available because of the 120° bond angles. In a trigonal bipyramidal electron-pair geometry, lone pairs always occupy equatorial positions because these more spacious positions can more easily accommodate the larger lone pairs.

Theoretically, we can come up with three possible arrangements for the three bonds and two lone pairs for the ClF_3 molecule ([\[link\]](#)). The stable structure is the one that puts the lone pairs in equatorial locations, giving a T-shaped molecular structure.



(a) In a trigonal bipyramid, the two axial positions are located directly across from one another, whereas the three equatorial positions are located in a triangular arrangement. (b–d) The two lone pairs (red lines) in ClF_3 have several possible arrangements, but the T-shaped molecular structure (b) is the one actually observed, consistent with the larger lone pairs both occupying equatorial positions.

When a central atom has two lone electron pairs and four bonding regions, we have an octahedral electron-pair geometry. The two lone pairs are on opposite sides of the octahedron (180° apart), giving a square planar molecular structure that minimizes lone pair-lone pair repulsions ([\[link\]](#)).

Predicting Electron Pair Geometry and Molecular Structure

The following procedure uses VSEPR theory to determine the electron pair geometries and the molecular structures:

1. Write the Lewis structure of the molecule or polyatomic ion.
2. Count the number of regions of electron density (lone pairs and bonds) around the central atom. A single, double, or triple bond counts as one region of electron density.
3. Identify the electron-pair geometry based on the number of regions of electron density: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral ([link](#), first column).
4. Use the number of lone pairs to determine the molecular structure ([link](#)). If more than one arrangement of lone pairs and chemical bonds is possible, choose the one that will minimize repulsions, remembering that lone pairs occupy more space than multiple bonds, which occupy more space than single bonds. In trigonal bipyramidal arrangements, repulsion is minimized when every lone pair is in an equatorial position. In an octahedral arrangement with two lone pairs, repulsion is minimized when the lone pairs are on opposite sides of the central atom.

The following examples illustrate the use of VSEPR theory to predict the molecular structure of molecules or ions that have no lone pairs of electrons. In this case, the molecular structure is identical to the electron pair geometry.

Example:

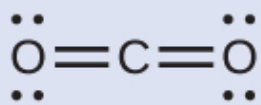
Predicting Electron-pair Geometry and Molecular Structure: CO₂ and BCl₃

Predict the electron-pair geometry and molecular structure for each of the following:

- (a) carbon dioxide, CO₂, a molecule produced by the combustion of fossil fuels
- (b) boron trichloride, BCl₃, an important industrial chemical

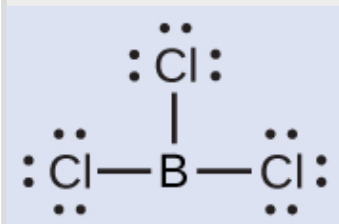
Solution

- (a) We write the Lewis structure of CO₂ as:

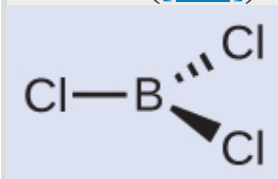


This shows us two regions of high electron density around the carbon atom—each double bond counts as one region, and there are no lone pairs on the carbon atom. Using VSEPR theory, we predict that the two regions of electron density arrange themselves on opposite sides of the central atom with a bond angle of 180° . The electron-pair geometry and molecular structure are identical, and CO_2 molecules are linear.

(b) We write the Lewis structure of BCl_3 as:



Thus we see that BCl_3 contains three bonds, and there are no lone pairs of electrons on boron. The arrangement of three regions of high electron density gives a trigonal planar electron-pair geometry. The B–Cl bonds lie in a plane with 120° angles between them. BCl_3 also has a trigonal planar molecular structure ([link](#)).



The electron-pair geometry and molecular structure of BCl_3 are both trigonal planar. Note that the VSEPR geometry indicates the correct bond angles (120°), unlike the Lewis structure shown above.

Check Your Learning

Carbonate, CO_3^{2-} , is a common polyatomic ion found in various materials from eggshells to antacids. What are the electron-pair geometry and molecular structure of this polyatomic ion?

Note:

Answer:

The electron-pair geometry is trigonal planar and the molecular structure is trigonal planar. Due to resonance, all three C–O bonds are identical. Whether they are single, double, or an average of the two, each bond counts as one region of electron density.

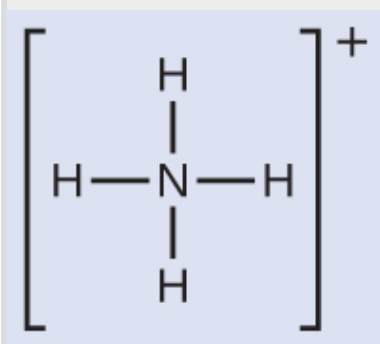
Example:**Predicting Electron-pair Geometry and Molecular Structure: Ammonium**

Two of the top 50 chemicals produced in the United States, ammonium nitrate and ammonium sulfate, both used as fertilizers, contain the ammonium ion.

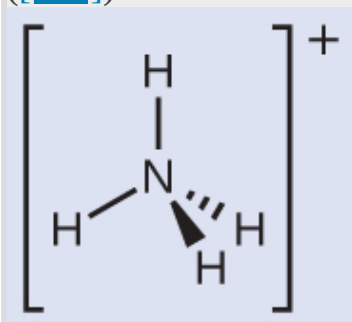
Predict the electron-pair geometry and molecular structure of the NH_4^+ cation.

Solution

We write the Lewis structure of NH_4^+ as:



We can see that NH_4^+ contains four bonds from the nitrogen atom to hydrogen atoms and no lone pairs. We expect the four regions of high electron density to arrange themselves so that they point to the corners of a tetrahedron with the central nitrogen atom in the middle ([link](#)). Therefore, the electron pair geometry of NH_4^+ is tetrahedral, and the molecular structure is also tetrahedral ([link](#)).



The ammonium
ion displays a
tetrahedral

electron-pair
geometry as well
as a tetrahedral
molecular
structure.

Check Your Learning

Identify a molecule with trigonal bipyramidal molecular structure.

Note:

Answer:

Any molecule with five electron pairs around the central atoms including no lone pairs will be trigonal bipyramidal. PF_5 is a common example.

The next several examples illustrate the effect of lone pairs of electrons on molecular structure.

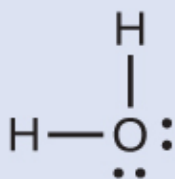
Example:

Predicting Electron-pair Geometry and Molecular Structure: Lone Pairs on the Central Atom

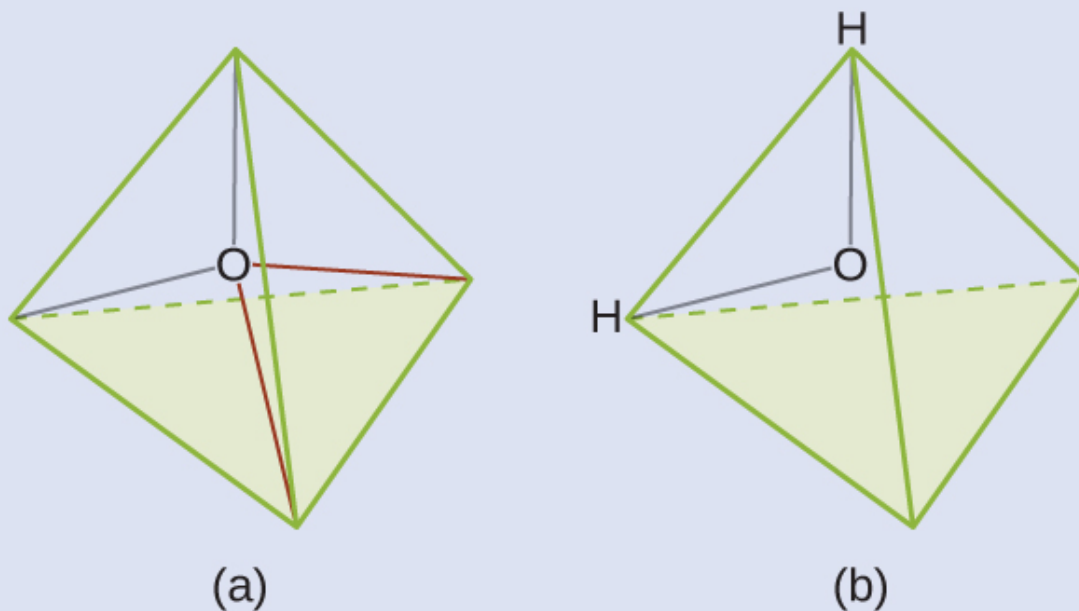
Predict the electron-pair geometry and molecular structure of a water molecule.

Solution

The Lewis structure of H_2O indicates that there are four regions of high electron density around the oxygen atom: two lone pairs and two chemical bonds:



We predict that these four regions are arranged in a tetrahedral fashion ([link](#)), as indicated in [link](#). Thus, the electron-pair geometry is tetrahedral and the molecular structure is bent with an angle slightly less than 109.5° . In fact, the bond angle is 104.5° .



(a) H_2O has four regions of electron density around the central atom, so it has a tetrahedral electron-pair geometry. (b) Two of the electron regions are lone pairs, so the molecular structure is bent.

Check Your Learning

The hydronium ion, H_3O^+ , forms when acids are dissolved in water. Predict the electron-pair geometry and molecular structure of this cation.

Note:

Answer:

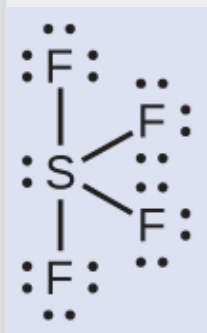
electron pair geometry: tetrahedral; molecular structure: trigonal pyramidal

Example:**Predicting Electron-pair Geometry and Molecular Structure: SF₄**

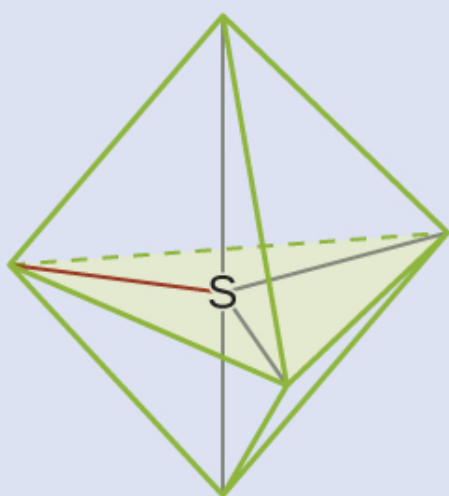
Sulfur tetrafluoride, SF₄, is extremely valuable for the preparation of fluorine-containing compounds used as herbicides (i.e., SF₄ is used as a fluorinating agent). Predict the electron-pair geometry and molecular structure of a SF₄ molecule.

Solution

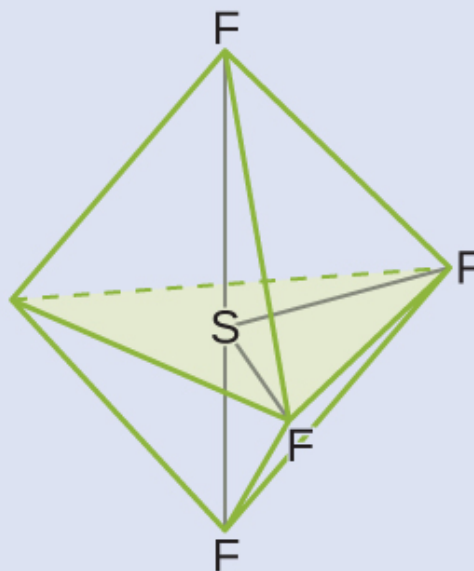
The Lewis structure of SF₄ indicates five regions of electron density around the sulfur atom: one lone pair and four bonding pairs:



We expect these five regions to adopt a trigonal bipyramidal electron-pair geometry. To minimize lone pair repulsions, the lone pair occupies one of the equatorial positions. The molecular structure ([\[link\]](#)) is that of a seesaw ([\[link\]](#)).



(a)



(b)

(a) SF₄ has a trigonal bipyramidal arrangement of the five regions of electron density. (b) One of the regions is a lone pair, which results in a seesaw-shaped molecular structure.

Check Your Learning

Predict the electron pair geometry and molecular structure for molecules of XeF₂.

Note:

Answer:

The electron-pair geometry is trigonal bipyramidal. The molecular structure is linear.

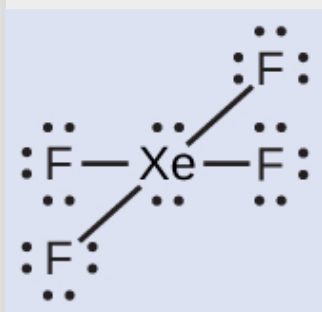
Example:

Predicting Electron-pair Geometry and Molecular Structure: XeF₄

Of all the noble gases, xenon is the most reactive, frequently reacting with elements such as oxygen and fluorine. Predict the electron-pair geometry and molecular structure of the XeF₄ molecule.

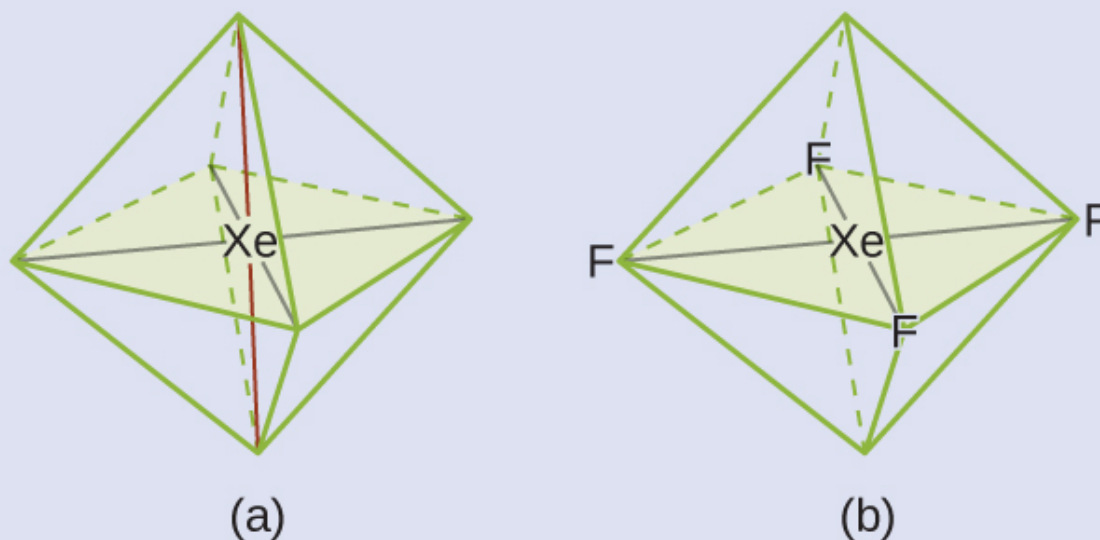
Solution

The Lewis structure of XeF₄ indicates six regions of high electron density around the xenon atom: two lone pairs and four bonds:



These six regions adopt an octahedral arrangement ([link](#)), which is the electron-pair geometry. To minimize repulsions, the lone pairs should be on

opposite sides of the central atom ([link](#)). The five atoms are all in the same plane and have a square planar molecular structure.



(a) XeF₄ adopts an octahedral arrangement with two lone pairs (red lines) and four bonds in the electron-pair geometry. (b) The molecular structure is square planar with the lone pairs directly across from one another.

Check Your Learning

In a certain molecule, the central atom has three lone pairs and two bonds. What will the electron pair geometry and molecular structure be?

Note:

Answer:

electron pair geometry: trigonal bipyramidal; molecular structure: linear

Molecular Structure for Multicenter Molecules

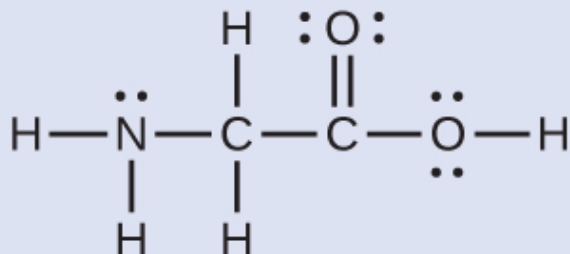
When a molecule or polyatomic ion has only one central atom, the molecular structure completely describes the shape of the molecule. Larger molecules do

not have a single central atom, but are connected by a chain of interior atoms that each possess a “local” geometry. The way these local structures are oriented with respect to each other also influences the molecular shape, but such considerations are largely beyond the scope of this introductory discussion. For our purposes, we will only focus on determining the local structures.

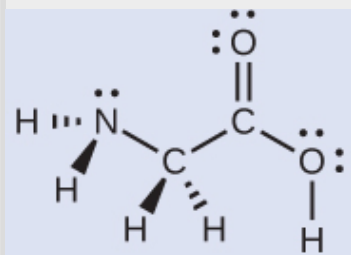
Example:

Predicting Structure in Multicenter Molecules

The Lewis structure for the simplest amino acid, glycine, $\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$, is shown here. Predict the local geometry for the nitrogen atom, the two carbon atoms, and the oxygen atom with a hydrogen atom attached:



Solution



Consider each central atom independently. The electron-pair geometries:

- nitrogen—four regions of electron density; tetrahedral
- carbon (CH_2)—four regions of electron density; tetrahedral
- carbon (CO_2)—three regions of electron density; trigonal planar
- oxygen (OH)—four regions of electron density; tetrahedral

The local structures:

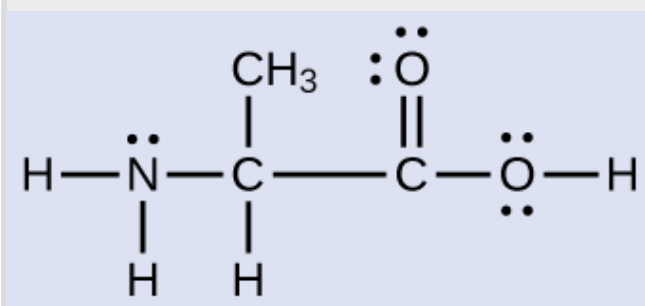
- nitrogen—three bonds, one lone pair; trigonal pyramidal

- carbon ($\underline{\text{C}}\text{H}_2$)—four bonds, no lone pairs; tetrahedral
- carbon ($\underline{\text{C}}\text{O}_2$)—three bonds (double bond counts as one bond), no lone pairs; trigonal planar
- oxygen ($\underline{\text{O}}\text{H}$)—two bonds, two lone pairs; bent (109°)

Check Your Learning

Another amino acid is alanine, which has the Lewis structure shown here.

Predict the electron-pair geometry and local structure of the nitrogen atom, the three carbon atoms, and the oxygen atom with hydrogen attached:



Note:

Answer:

electron-pair geometries: nitrogen—tetrahedral; carbon ($\underline{\text{C}}\text{H}$)—tetrahedral; carbon ($\underline{\text{C}}\text{H}_3$)—tetrahedral; carbon ($\underline{\text{C}}\text{O}_2$)—trigonal planar; oxygen ($\underline{\text{O}}\text{H}$)—tetrahedral; local structures: nitrogen—trigonal pyramidal; carbon ($\underline{\text{C}}\text{H}$)—tetrahedral; carbon ($\underline{\text{C}}\text{H}_3$)—tetrahedral; carbon ($\underline{\text{C}}\text{O}_2$)—trigonal planar; oxygen ($\underline{\text{O}}\text{H}$)—bent (109°)

Note:

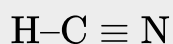


The [molecular shape simulator](#) lets you build various molecules and practice naming their electron-pair geometries and molecular structures.

Example:**Molecular Simulation**

Using [molecular shape simulator](#) allows us to control whether bond angles and/or lone pairs are displayed by checking or unchecking the boxes under “Options” on the right. We can also use the “Name” checkboxes at bottom-left to display or hide the electron pair geometry (called “electron geometry” in the simulator) and/or molecular structure (called “molecular shape” in the simulator).

Build the molecule HCN in the simulator based on the following Lewis structure:

Equation:

Click on each bond type or lone pair at right to add that group to the central atom. Once you have the complete molecule, rotate it to examine the predicted molecular structure. What molecular structure is this?

Solution

The molecular structure is linear.

Check Your Learning

Build a more complex molecule in the simulator. Identify the electron-group geometry, molecular structure, and bond angles. Then try to find a chemical formula that would match the structure you have drawn.

Note:**Answer:**

Answers will vary. For example, an atom with four single bonds, a double bond, and a lone pair has an octahedral electron-group geometry and a square pyramidal molecular structure. XeOF_4 is a molecule that adopts this structure.

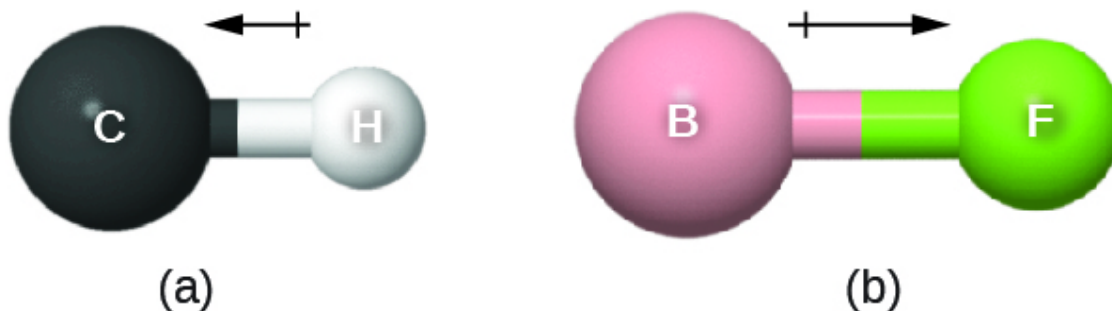
Molecular Polarity and Dipole Moment

As discussed previously, polar covalent bonds connect two atoms with differing electronegativities, leaving one atom with a partial positive charge (δ^+) and the other atom with a partial negative charge (δ^-), as the electrons are pulled toward the more electronegative atom. This separation of charge gives rise to a **bond dipole moment**. The magnitude of a bond dipole moment is represented by the Greek letter mu (μ) and is given by the formula shown here, where Q is the magnitude of the partial charges (determined by the electronegativity difference) and r is the distance between the charges:

Equation:

$$\mu = Qr$$

This bond moment can be represented as a **vector**, a quantity having both direction and magnitude ([\[link\]](#)). Dipole vectors are shown as arrows pointing along the bond from the less electronegative atom toward the more electronegative atom. A small plus sign is drawn on the less electronegative end to indicate the partially positive end of the bond. The length of the arrow is proportional to the magnitude of the electronegativity difference between the two atoms.



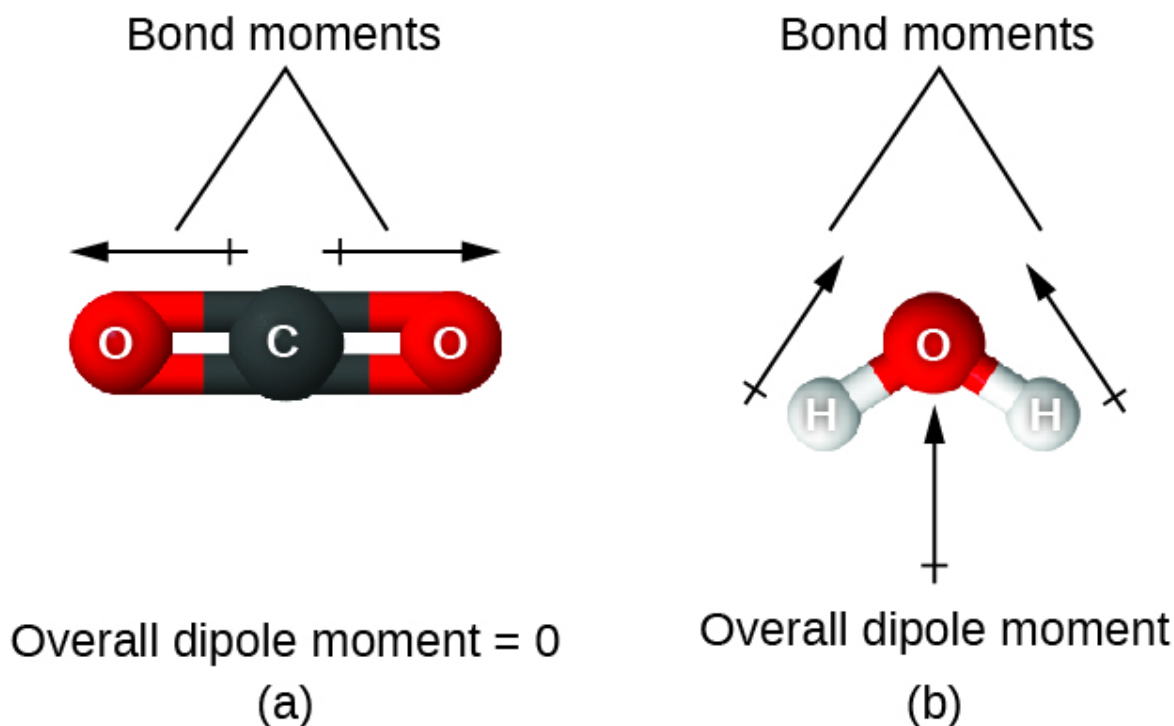
(a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegativity difference between B and F is much larger, so the vector representing the bond moment is much longer.

A whole molecule may also have a separation of charge, depending on its molecular structure and the polarity of each of its bonds. If such a charge separation exists, the molecule is said to be a **polar molecule** (or dipole); otherwise the molecule is said to be nonpolar. The **dipole moment** measures the extent of net charge separation in the molecule as a whole. We determine the dipole moment by adding the bond moments in three-dimensional space, taking into account the molecular structure.

For diatomic molecules, there is only one bond, so its bond dipole moment determines the molecular polarity. Homonuclear diatomic molecules such as Br_2 and N_2 have no difference in electronegativity, so their dipole moment is zero. For heteronuclear molecules such as CO , there is a small dipole moment. For HF , there is a larger dipole moment because there is a larger difference in electronegativity.

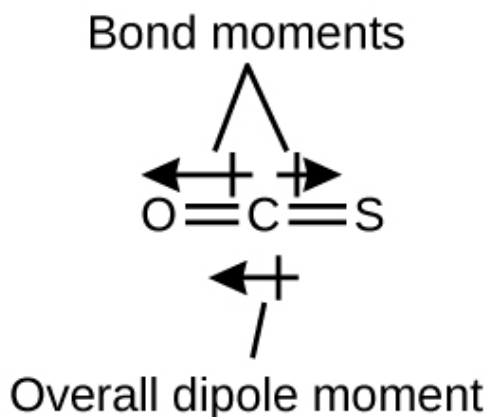
When a molecule contains more than one bond, the geometry must be taken into account. If the bonds in a molecule are arranged such that their bond moments cancel (vector sum equals zero), then the molecule is nonpolar. This is the situation in CO_2 ([link](#)). Each of the bonds is polar, but the molecule as a whole is nonpolar. From the Lewis structure, and using VSEPR theory, we determine that the CO_2 molecule is linear with polar $\text{C}=\text{O}$ bonds on opposite sides of the carbon atom. The bond moments cancel because they are pointed in opposite directions. In the case of the water molecule ([link](#)), the Lewis structure again shows that there are two bonds to a central atom, and the electronegativity

difference again shows that each of these bonds has a nonzero bond moment. In this case, however, the molecular structure is bent because of the lone pairs on O, and the two bond moments do not cancel. Therefore, water does have a net dipole moment and is a polar molecule (dipole).



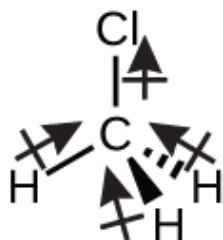
The overall dipole moment of a molecule depends on the individual bond dipole moments and how they are arranged. (a) Each CO bond has a bond dipole moment, but they point in opposite directions so that the net CO₂ molecule is nonpolar. (b) In contrast, water is polar because the OH bond moments do not cancel out.

The OCS molecule has a structure similar to CO₂, but a sulfur atom has replaced one of the oxygen atoms. To determine if this molecule is polar, we draw the molecular structure. VSEPR theory predicts a linear molecule:

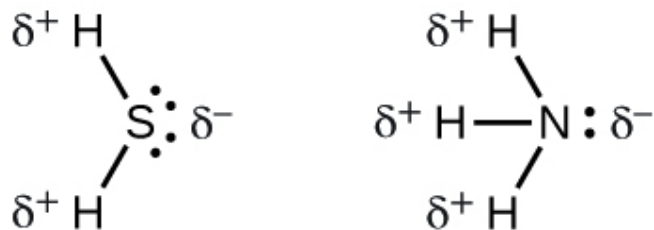


The C-O bond is considerably polar. Although C and S have very similar electronegativity values, S is slightly more electronegative than C, and so the C-S bond is just slightly polar. Because oxygen is more electronegative than sulfur, the oxygen end of the molecule is the negative end.

Chloromethane, CH_3Cl , is another example of a polar molecule. Although the polar C-Cl and C-H bonds are arranged in a tetrahedral geometry, the C-Cl bonds have a larger bond moment than the C-H bond, and the bond moments do not completely cancel each other. All of the dipoles have an upward component in the orientation shown, since carbon is more electronegative than hydrogen and less electronegative than chlorine:



When we examine the highly symmetrical molecules BF_3 (trigonal planar), CH_4 (tetrahedral), PF_5 (trigonal bipyramidal), and SF_6 (octahedral), in which all the polar bonds are identical, the molecules are nonpolar. The bonds in these molecules are arranged such that their dipoles cancel. However, just because a molecule contains identical bonds does not mean that the dipoles will always cancel. Many molecules that have identical bonds and lone pairs on the central atoms have bond dipoles that do not cancel. Examples include H_2S and NH_3 . A hydrogen atom is at the positive end and a nitrogen or sulfur atom is at the negative end of the polar bonds in these molecules:

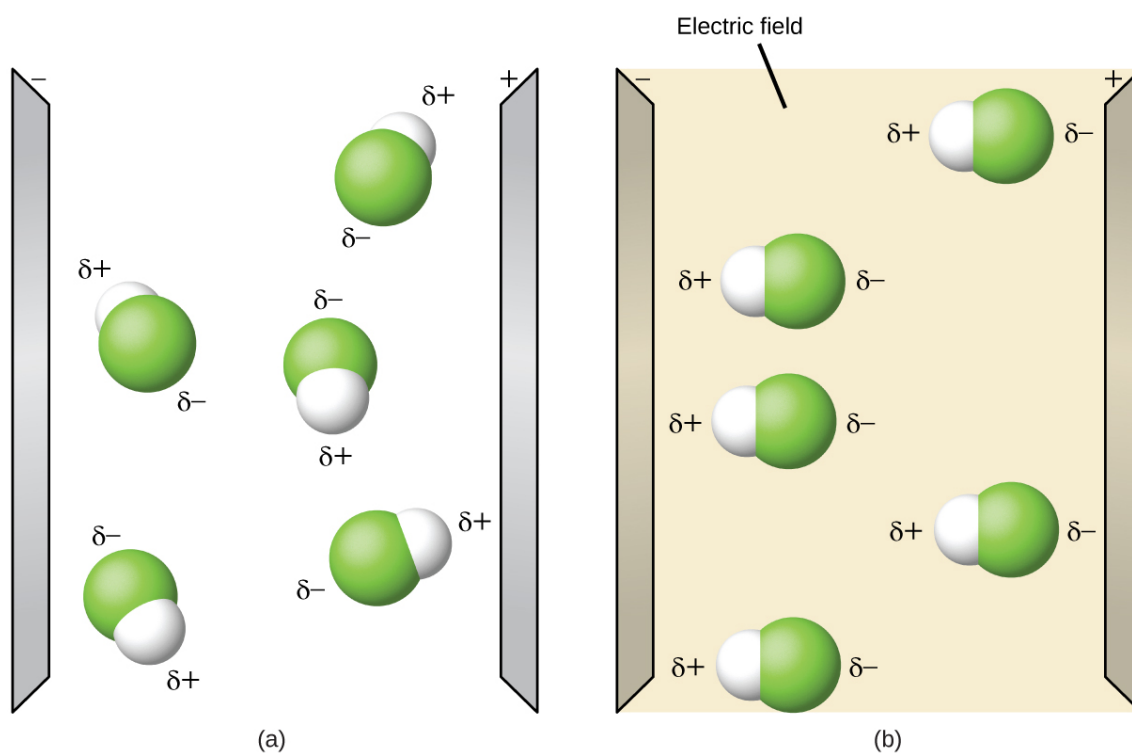


To summarize, to be polar, a molecule must:

1. Contain at least one polar covalent bond.
2. Have a molecular structure such that the sum of the vectors of each bond dipole moment does not cancel.

Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate ([link](#)). We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.



(a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction.

Note:



The [molecule polarity simulation](#) provides many ways to explore dipole moments of bonds and molecules.

Example:**Polarity Simulations**

Open the [molecule polarity simulation](#) and select the “Three Atoms” tab at the top. This should display a molecule ABC with three electronegativity adjusters. You can display or hide the bond moments, molecular dipoles, and partial charges at the right. Turning on the Electric Field will show whether the molecule moves when exposed to a field, similar to [\[link\]](#).

Use the electronegativity controls to determine how the molecular dipole will look for the starting bent molecule if:

- (a) A and C are very electronegative and B is in the middle of the range.
- (b) A is very electronegative, and B and C are not.

Solution

- (a) Molecular dipole moment points immediately between A and C.
- (b) Molecular dipole moment points along the A–B bond, toward A.

Check Your Learning

Determine the partial charges that will give the largest possible bond dipoles.

Note:**Answer:**

The largest bond moments will occur with the largest partial charges. The two solutions above represent how unevenly the electrons are shared in the bond. The bond moments will be maximized when the electronegativity difference is greatest. The controls for A and C should be set to one extreme, and B should be set to the opposite extreme. Although the magnitude of the bond moment will not change based on whether B is the most electronegative or the least, the direction of the bond moment will.

Key Concepts and Summary

VSEPR theory predicts the three-dimensional arrangement of atoms in a molecule. It states that valence electrons will assume an electron-pair geometry that minimizes repulsions between areas of high electron density (bonds and/or lone pairs). Molecular structure, which refers only to the placement of atoms in

a molecule and not the electrons, is equivalent to electron-pair geometry only when there are no lone electron pairs around the central atom. A dipole moment measures a separation of charge. For one bond, the bond dipole moment is determined by the difference in electronegativity between the two atoms. For a molecule, the overall dipole moment is determined by both the individual bond moments and how these dipoles are arranged in the molecular structure. Polar molecules (those with an appreciable dipole moment) interact with electric fields, whereas nonpolar molecules do not.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Explain why the HOH molecule is bent, whereas the HBeH molecule is linear.

Solution:

The placement of the two sets of unpaired electrons in water forces the bonds to assume a tetrahedral arrangement, and the resulting HOH molecule is bent. The HBeH molecule (in which Be has only two electrons to bond with the two electrons from the hydrogens) must have the electron pairs as far from one another as possible and is therefore linear.

Exercise:

Problem:

What feature of a Lewis structure can be used to tell if a molecule's (or ion's) electron-pair geometry and molecular structure will be identical?

Exercise:

Problem:

Explain the difference between electron-pair geometry and molecular structure.

Solution:

Space must be provided for each pair of electrons whether they are in a bond or are present as lone pairs. Electron-pair geometry considers the placement of all electrons. Molecular structure considers only the bonding-pair geometry.

Exercise:

Problem:

Why is the H–N–H angle in NH_3 smaller than the H–C–H bond angle in CH_4 ? Why is the H–N–H angle in NH_4^+ identical to the H–C–H bond angle in CH_4 ?

Exercise:

Problem:

Explain how a molecule that contains polar bonds can be nonpolar.

Solution:

As long as the polar bonds are compensated (for example, two identical atoms are found directly across the central atom from one another), the molecule can be nonpolar.

Exercise:

Problem:

As a general rule, MX_n molecules (where M represents a central atom and X represents terminal atoms; $n = 2 - 5$) are polar if there is one or more lone pairs of electrons on M. NH_3 (M = N, X = H, $n = 3$) is an example. There are two molecular structures with lone pairs that are exceptions to this rule. What are they?

Exercise:

Problem:

Predict the electron pair geometry and the molecular structure of each of the following molecules or ions:

(a) SF_6

(b) PCl_5



Solution:

(a) Both the electron geometry and the molecular structure are octahedral.

(b) Both the electron geometry and the molecular structure are trigonal bipyramid.

(c) Both the electron geometry and the molecular structure are linear.

(d) Both the electron geometry and the molecular structure are trigonal planar.

Exercise:

Problem:

Identify the electron pair geometry and the molecular structure of each of the following molecules or ions:



Exercise:

Problem:

What are the electron-pair geometry and the molecular structure of each of the following molecules or ions?



(d) PCl_3

(e) SeF_4

(f) PH_2^-

Solution:

(a) electron-pair geometry: octahedral, molecular structure: square pyramidal; (b) electron-pair geometry: tetrahedral, molecular structure: bent; (c) electron-pair geometry: octahedral, molecular structure: square planar; (d) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal; (e) electron-pair geometry: trigonal bipyramidal, molecular structure: seesaw; (f) electron-pair geometry: tetrahedral, molecular structure: bent (109°)

Exercise:

Problem:

Predict the electron pair geometry and the molecular structure of each of the following ions:

(a) H_3O^+

(b) PCl_4^-

(c) SnCl_3^-

(d) BrCl_4^-

(e) ICl_3

(f) XeF_4

(g) SF_2

Exercise:

Problem:

Identify the electron pair geometry and the molecular structure of each of the following molecules:

- (a) ClNO (N is the central atom)
 - (b) CS_2
 - (c) Cl_2CO (C is the central atom)
 - (d) Cl_2SO (S is the central atom)
 - (e) SO_2F_2 (S is the central atom)
 - (f) XeO_2F_2 (Xe is the central atom)
 - (g) ClOF_2^+ (Cl is the central atom)
-

Solution:

(a) electron-pair geometry: trigonal planar, molecular structure: bent (120°); (b) electron-pair geometry: linear, molecular structure: linear; (c) electron-pair geometry: trigonal planar, molecular structure: trigonal planar; (d) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal; (e) electron-pair geometry: tetrahedral, molecular structure: tetrahedral; (f) electron-pair geometry: trigonal bipyramidal, molecular structure: seesaw; (g) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal

Exercise:

Problem:

Predict the electron pair geometry and the molecular structure of each of the following:

- (a) IOF_5 (I is the central atom)
- (b) POCl_3 (P is the central atom)
- (c) Cl_2SeO (Se is the central atom)
- (d) ClSO^+ (S is the central atom)
- (e) F_2SO (S is the central atom)



Exercise:

Problem:

Which of the following molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?



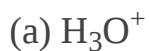
Solution:

All of these molecules and ions contain polar bonds. Only ClF_5 , ClO_2^- , PCl_3 , SeF_4 , and PH_2^- have dipole moments.

Exercise:

Problem:

Which of these molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?





Exercise:

Problem: Which of the following molecules have dipole moments?

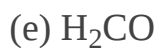
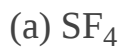


Solution:

SeS_2 , CCl_2F_2 , PCl_3 , and ClNO all have dipole moments.

Exercise:

Problem: Identify the molecules with a dipole moment:



Exercise:

Problem:

The molecule XF_3 has a dipole moment. Is X boron or phosphorus?

Solution:

P

Exercise:**Problem:**

The molecule XCl_2 has a dipole moment. Is X beryllium or sulfur?

Exercise:

Problem: Is the Cl_2BBCl_2 molecule polar or nonpolar?

Solution:

nonpolar

Exercise:**Problem:**

There are three possible structures for PCl_2F_3 with phosphorus as the central atom. Draw them and discuss how measurements of dipole moments could help distinguish among them.

Exercise:**Problem:**

Describe the molecular structure around the indicated atom or atoms:

(a) the sulfur atom in sulfuric acid, H_2SO_4 [$(\text{HO})_2\text{SO}_2$]

(b) the chlorine atom in chloric acid, HClO_3 [HOClO_2]

(c) the oxygen atom in hydrogen peroxide, HOOH

(d) the nitrogen atom in nitric acid, HNO_3 [HONO_2]

- (e) the oxygen atom in the OH group in nitric acid, HNO_3 [HONO_2]
(f) the central oxygen atom in the ozone molecule, O_3
(g) each of the carbon atoms in propyne, CH_3CCH
(h) the carbon atom in Freon, CCl_2F_2
(i) each of the carbon atoms in allene, H_2CCCH_2
-

Solution:

- (a) tetrahedral; (b) trigonal pyramidal; (c) bent (109°); (d) trigonal planar;
(e) bent (109°); (f) bent (109°); (g) $\underline{\text{C}}\text{H}_3\text{CCH}$ tetrahedral, $\text{CH}_3\underline{\text{C}}\underline{\text{C}}\text{H}$ linear;
(h) tetrahedral; (i) $\text{H}_2\underline{\text{C}}\underline{\text{C}}\text{CH}_2$ linear; $\text{H}_2\underline{\text{C}}\underline{\text{C}}\underline{\text{C}}\text{H}_2$ trigonal planar

Exercise:

Problem:

Draw the Lewis structures and predict the shape of each compound or ion:

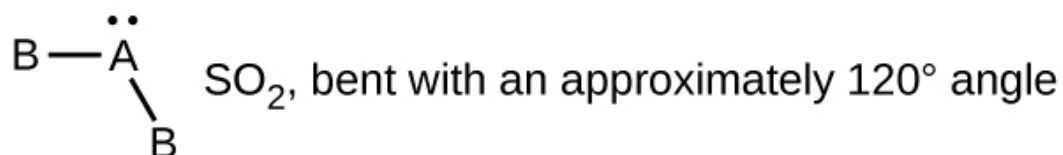
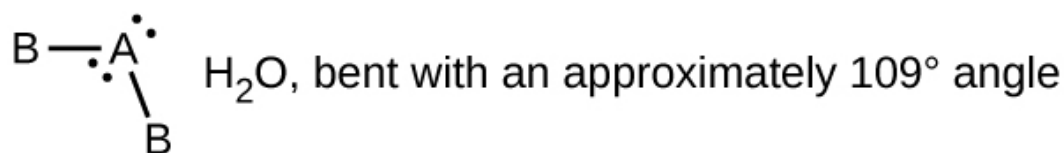
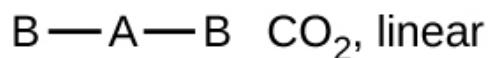
- (a) CO_2
(b) NO_2^-
(c) SO_3
(d) SO_3^{2-}

Exercise:

Problem:

A molecule with the formula AB_2 , in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion for each shape.

Solution:



Exercise:

Problem:

A molecule with the formula AB_3 , in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion that has each shape.

Exercise:

Problem:

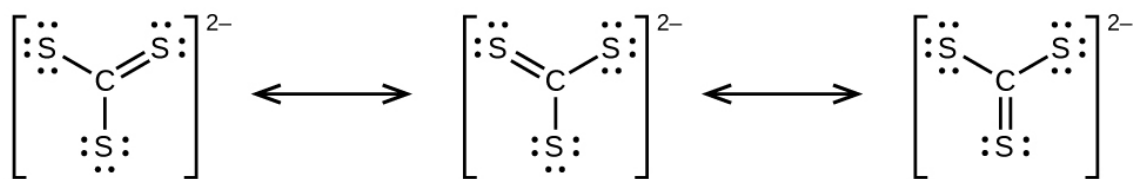
Draw the Lewis electron dot structures for these molecules, including resonance structures where appropriate:



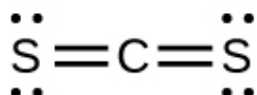
(d) predict the molecular shapes for CS_3^{2-} and CS_2 and explain how you arrived at your predictions

Solution:

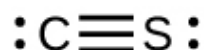
(a)



;
(b)



;
(c)



;
(d) CS_3^{2-} includes three regions of electron density (all are bonds with no lone pairs); the shape is trigonal planar; CS_2 has only two regions of electron density (all bonds with no lone pairs); the shape is linear

Exercise:

Problem:

What is the molecular structure of the stable form of FNO_2 ? (N is the central atom.)

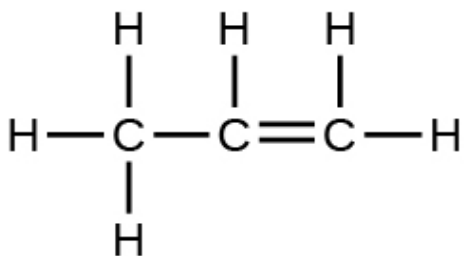
Exercise:

Problem:

A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen. What is its molecular structure?

Solution:

The Lewis structure is made from three units, but the atoms must be rearranged:



Exercise:

Problem:

Use the [simulation](#) to perform the following exercises for a two-atom molecule:

- (a) Adjust the electronegativity value so the bond dipole is pointing toward B. Then determine what the electronegativity values must be to switch the dipole so that it points toward A.
- (b) With a partial positive charge on A, turn on the electric field and describe what happens.
- (c) With a small partial negative charge on A, turn on the electric field and describe what happens.
- (d) Reset all, and then with a large partial negative charge on A, turn on the electric field and describe what happens.

Exercise:

Problem:

Use the [simulation](#) to perform the following exercises for a real molecule. You may need to rotate the molecules in three dimensions to see certain dipoles.

- (a) Sketch the bond dipoles and molecular dipole (if any) for O₃. Explain your observations.
- (b) Look at the bond dipoles for NH₃. Use these dipoles to predict whether N or H is more electronegative.

(c) Predict whether there should be a molecular dipole for NH_3 and, if so, in which direction it will point. Check the molecular dipole box to test your hypothesis.

Solution:

The molecular dipole points away from the hydrogen atoms.

Exercise:

Problem:

Use the [Molecule Shape simulator](#) to build a molecule. Starting with the central atom, click on the double bond to add one double bond. Then add one single bond and one lone pair. Rotate the molecule to observe the complete geometry. Name the electron group geometry and molecular structure and predict the bond angle. Then click the check boxes at the bottom and right of the simulator to check your answers.

Exercise:

Problem:

Use the [Molecule Shape simulator](#) to explore real molecules. On the Real Molecules tab, select H_2O . Switch between the “real” and “model” modes. Explain the difference observed.

Solution:

The structures are very similar. In the model mode, each electron group occupies the same amount of space, so the bond angle is shown as 109.5° . In the “real” mode, the lone pairs are larger, causing the hydrogens to be compressed. This leads to the smaller angle of 104.5° .

Exercise:

Problem:

Use the [Molecule Shape simulator](#) to explore real molecules. On the Real Molecules tab, select “model” mode and S_2O . What is the model bond angle? Explain whether the “real” bond angle should be larger or smaller than the ideal model angle.

Glossary

axial position

location in a trigonal bipyramidal geometry in which there is another atom at a 180° angle and the equatorial positions are at a 90° angle

bond angle

angle between any two covalent bonds that share a common atom

bond distance

(also, bond length) distance between the nuclei of two bonded atoms

bond dipole moment

separation of charge in a bond that depends on the difference in electronegativity and the bond distance represented by partial charges or a vector

dipole moment

property of a molecule that describes the separation of charge determined by the sum of the individual bond moments based on the molecular structure

electron-pair geometry

arrangement around a central atom of all regions of electron density (bonds, lone pairs, or unpaired electrons)

equatorial position

one of the three positions in a trigonal bipyramidal geometry with 120° angles between them; the axial positions are located at a 90° angle

linear

shape in which two outside groups are placed on opposite sides of a central atom

molecular structure

structure that includes only the placement of the atoms in the molecule

octahedral

shape in which six outside groups are placed around a central atom such that a three-dimensional shape is generated with four groups forming a

square and the other two forming the apex of two pyramids, one above and one below the square plane

polar molecule

(also, dipole) molecule with an overall dipole moment

tetrahedral

shape in which four outside groups are placed around a central atom such that a three-dimensional shape is generated with four corners and 109.5° angles between each pair and the central atom

trigonal bipyramidal

shape in which five outside groups are placed around a central atom such that three form a flat triangle with 120° angles between each pair and the central atom, and the other two form the apex of two pyramids, one above and one below the triangular plane

trigonal planar

shape in which three outside groups are placed in a flat triangle around a central atom with 120° angles between each pair and the central atom

valence shell electron-pair repulsion theory (VSEPR)

theory used to predict the bond angles in a molecule based on positioning regions of high electron density as far apart as possible to minimize electrostatic repulsion

vector

quantity having magnitude and direction

Introduction

class="introduction"

- Energy Basics
- Calorimetry
- Enthalpy

Sliding a
match head
along a
rough
surface
initiates a
combustion
reaction that
produces
energy in
the form of
heat and
light.
(credit:
modificatio
n of work
by Laszlo
Ilyes)



Chemical reactions, such as those that occur when you light a match, involve changes in energy as well as matter. Societies at all levels of development could not function without the energy released by chemical reactions. In 2012, about 85% of US energy consumption came from the combustion of petroleum products, coal, wood, and garbage. We use this energy to produce electricity (38%); to transport food, raw materials, manufactured goods, and people (27%); for industrial production (21%); and to heat and power our homes and businesses (10%).[\[footnote\]](#) While these combustion reactions help us meet our essential energy needs, they are also recognized by the majority of the scientific community as a major contributor to global climate change.

US Energy Information Administration, *Primary Energy Consumption by Source and Sector*, 2012,

http://www.eia.gov/totalenergy/data/monthly/pdf/flow/css_2012_energy.pdf
. Data derived from US Energy Information Administration, *Monthly Energy Review* (January 2014).

Useful forms of energy are also available from a variety of chemical reactions other than combustion. For example, the energy produced by the batteries in a cell phone, car, or flashlight results from chemical reactions. This chapter introduces many of the basic ideas necessary to explore the relationships between chemical changes and energy, with a focus on thermal energy.

Energy Basics

By the end of this section, you will be able to:

- Define energy, distinguish types of energy, and describe the nature of energy changes that accompany chemical and physical changes
- Distinguish the related properties of heat, thermal energy, and temperature
- Define and distinguish specific heat and heat capacity, and describe the physical implications of both
- Perform calculations involving heat, specific heat, and temperature change

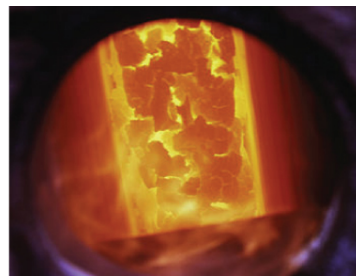
Chemical changes and their accompanying changes in energy are important parts of our everyday world ([\[link\]](#)). The macronutrients in food (proteins, fats, and carbohydrates) undergo metabolic reactions that provide the energy to keep our bodies functioning. We burn a variety of fuels (gasoline, natural gas, coal) to produce energy for transportation, heating, and the generation of electricity. Industrial chemical reactions use enormous amounts of energy to produce raw materials (such as iron and aluminum). Energy is then used to manufacture those raw materials into useful products, such as cars, skyscrapers, and bridges.



(a)



(b)



(c)

The energy involved in chemical changes is important to our daily lives: (a) A cheeseburger for lunch provides the energy you need to get through the rest of the day; (b) the combustion of gasoline provides the energy that moves your car (and you) between home, work, and school; and (c) coke, a processed form of coal, provides the energy needed to convert iron ore into iron, which is essential for making many of the products we use daily. (credit a: modification of work by

“Pink Sherbet Photography”/Flickr; credit b: modification of work by Jeffery Turner)

Over 90% of the energy we use comes originally from the sun. Every day, the sun provides the earth with almost 10,000 times the amount of energy necessary to meet all of the world’s energy needs for that day. Our challenge is to find ways to convert and store incoming solar energy so that it can be used in reactions or chemical processes that are both convenient and nonpolluting. Plants and many bacteria capture solar energy through photosynthesis. We release the energy stored in plants when we burn wood or plant products such as ethanol. We also use this energy to fuel our bodies by eating food that comes directly from plants or from animals that got their energy by eating plants. Burning coal and petroleum also releases stored solar energy: These fuels are fossilized plant and animal matter.

This chapter will introduce the basic ideas of an important area of science concerned with the amount of heat absorbed or released during chemical and physical changes—an area called **thermochemistry**. The concepts introduced in this chapter are widely used in almost all scientific and technical fields. Food scientists use them to determine the energy content of foods. Biologists study the energetics of living organisms, such as the metabolic combustion of sugar into carbon dioxide and water. The oil, gas, and transportation industries, renewable energy providers, and many others endeavor to find better methods to produce energy for our commercial and personal needs. Engineers strive to improve energy efficiency, find better ways to heat and cool our homes, refrigerate our food and drinks, and meet the energy and cooling needs of computers and electronics, among other applications. Understanding thermochemical principles is essential for chemists, physicists, biologists, geologists, every type of engineer, and just about anyone who studies or does any kind of science.

Energy

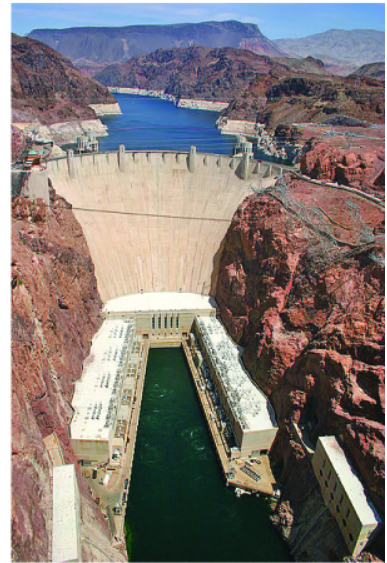
Energy can be defined as the capacity to supply heat or do work. One type of **work (w)** is the process of causing matter to move against an opposing force. For example, we do work when we inflate a bicycle tire—we move

matter (the air in the pump) against the opposing force of the air already in the tire.

Like matter, energy comes in different types. One scheme classifies energy into two types: **potential energy**, the energy an object has because of its relative position, composition, or condition, and **kinetic energy**, the energy that an object possesses because of its motion. Water at the top of a waterfall or dam has potential energy because of its position; when it flows downward through generators, it has kinetic energy that can be used to do work and produce electricity in a hydroelectric plant ([link](#)). A battery has potential energy because the chemicals within it can produce electricity that can do work.



(a)



(b)

(a) Water that is higher in elevation, for example, at the top of Victoria Falls, has a higher potential energy than water at a lower elevation. As the water falls, some of its potential energy is converted into kinetic energy. (b) If the water flows through generators at the bottom of a dam, such as the Hoover Dam shown here, its kinetic energy is converted into electrical energy. (credit a: modification of work by Steve Jurvetson; credit b: modification of work by “curimedia”/Wikimedia commons)

Energy can be converted from one form into another, but all of the energy present before a change occurs always exists in some form after the change is completed. This observation is expressed in the law of conservation of energy: during a chemical or physical change, energy can be neither created nor destroyed, although it can be changed in form. (This is also one version of the first law of thermodynamics, as you will learn later.)

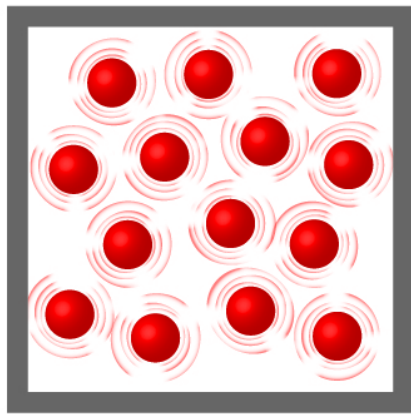
When one substance is converted into another, there is always an associated conversion of one form of energy into another. Heat is usually released or absorbed, but sometimes the conversion involves light, electrical energy, or some other form of energy. For example, chemical energy (a type of potential energy) is stored in the molecules that compose gasoline. When gasoline is combusted within the cylinders of a car's engine, the rapidly expanding gaseous products of this chemical reaction generate mechanical energy (a type of kinetic energy) when they move the cylinders' pistons.

According to the law of conservation of matter (seen in an earlier chapter), there is no detectable change in the total amount of matter during a chemical change. When chemical reactions occur, the energy changes are relatively modest and the mass changes are too small to measure, so the laws of conservation of matter and energy hold well. However, in nuclear reactions, the energy changes are much larger (by factors of a million or so), the mass changes are measurable, and matter-energy conversions are significant. This will be examined in more detail in a later chapter on nuclear chemistry. To encompass both chemical and nuclear changes, we combine these laws into one statement: The total quantity of matter and energy in the universe is fixed.

Thermal Energy, Temperature, and Heat

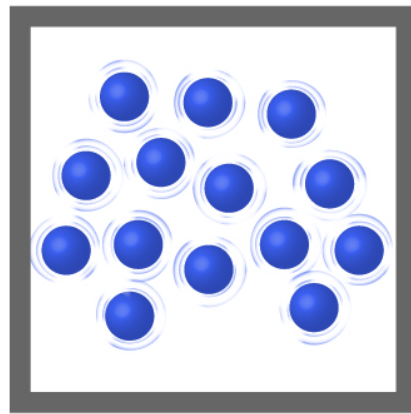
Thermal energy is kinetic energy associated with the random motion of atoms and molecules. **Temperature** is a quantitative measure of “hot” or “cold.” When the atoms and molecules in an object are moving or vibrating quickly, they have a higher average kinetic energy (KE), and we say that the

object is “hot.” When the atoms and molecules are moving slowly, they have lower average KE, and we say that the object is “cold” ([\[link\]](#)). Assuming that no chemical reaction or phase change (such as melting or vaporizing) occurs, increasing the amount of thermal energy in a sample of matter will cause its temperature to increase. And, assuming that no chemical reaction or phase change (such as condensation or freezing) occurs, decreasing the amount of thermal energy in a sample of matter will cause its temperature to decrease.



Hot water

(a)



Cold water

(b)

(a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.

Note:

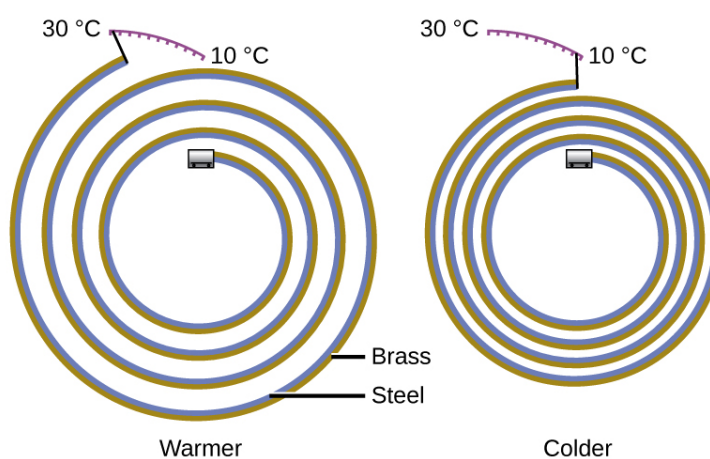


Click on this [interactive simulation](#) to view the effects of temperature on molecular motion.

Most substances expand as their temperature increases and contract as their temperature decreases. This property can be used to measure temperature changes, as shown in [\[link\]](#). The operation of many thermometers depends on the expansion and contraction of substances in response to temperature changes.



(a)



(b)

(a) In an alcohol or mercury thermometer, the liquid (dyed red for visibility) expands when heated and contracts when cooled, much more so than the glass tube that contains the liquid. (b) In a bimetallic thermometer, two different metals (such as brass and steel) form a two-layered strip. When heated or cooled, one of the metals (brass)

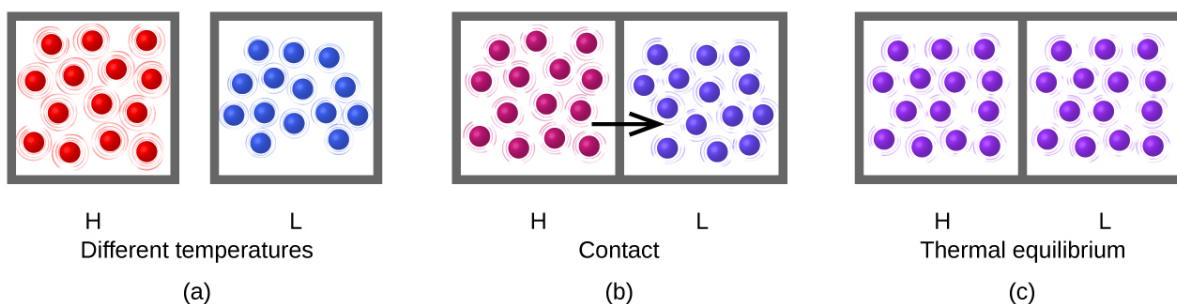
expands or contracts more than the other metal (steel), causing the strip to coil or uncoil. Both types of thermometers have a calibrated scale that indicates the temperature. (credit a: modification of work by “dwstucke”/Flickr)

Note:



The following [demonstration](#) allows one to view the effects of heating and cooling a coiled bimetallic strip.

Heat (q) is the transfer of thermal energy between two bodies at different temperatures. Heat flow (a redundant term, but one commonly used) increases the thermal energy of one body and decreases the thermal energy of the other. Suppose we initially have a high temperature (and high thermal energy) substance (H) and a low temperature (and low thermal energy) substance (L). The atoms and molecules in H have a higher average KE than those in L. If we place substance H in contact with substance L, the thermal energy will flow spontaneously from substance H to substance L. The temperature of substance H will decrease, as will the average KE of its molecules; the temperature of substance L will increase, along with the average KE of its molecules. Heat flow will continue until the two substances are at the same temperature ([\[link\]](#)).



(a) Substances H and L are initially at different temperatures, and their atoms have different average kinetic energies. (b) When they are put into contact with each other, collisions between the molecules result in the transfer of kinetic (thermal) energy from the hotter to the cooler matter. (c) The two objects reach “thermal equilibrium” when both substances are at the same temperature, and their molecules have the same average kinetic energy.

Note:



Click on the [PhET simulation](#) to explore energy forms and changes. Visit the Energy Systems tab to create combinations of energy sources, transformation methods, and outputs. Click on Energy Symbols to visualize the transfer of energy.

Matter undergoing chemical reactions and physical changes can release or absorb heat. A change that releases heat is called an **exothermic process**.

For example, the combustion reaction that occurs when using an oxyacetylene torch is an exothermic process—this process also releases energy in the form of light as evidenced by the torch's flame ([link](#)). A reaction or change that absorbs heat is an **endothermic process**. A cold pack used to treat muscle strains provides an example of an endothermic process. When the substances in the cold pack (water and a salt like ammonium nitrate) are brought together, the resulting process absorbs heat, leading to the sensation of cold.



(a)



(b)

(a) An oxyacetylene torch produces heat by the combustion of acetylene in oxygen. The energy released by this exothermic reaction heats and then melts the metal being cut. The sparks are tiny bits of the molten metal flying away. (b) A cold pack uses an endothermic process to create the sensation of cold. (credit a: modification of work by “Skatebiker”/Wikimedia commons)

Historically, energy was measured in units of **calories (cal)**. A calorie is the amount of energy required to raise one gram of water by 1 degree C (1 kelvin). However, this quantity depends on the atmospheric pressure and the starting temperature of the water. The ease of measurement of energy changes in calories has meant that the calorie is still frequently used. The

Calorie (with a capital C), or large calorie, commonly used in quantifying food energy content, is a kilocalorie. The SI unit of heat, work, and energy is the joule. A **joule (J)** is defined as the amount of energy used when a force of 1 newton moves an object 1 meter. It is named in honor of the English physicist James Prescott Joule. One joule is equivalent to 1 kg m²/s², which is also called 1 newton–meter. A kilojoule (kJ) is 1000 joules. To standardize its definition, 1 calorie has been set to equal 4.184 joules.

We now introduce two concepts useful in describing heat flow and temperature change. The **heat capacity (C)** of a body of matter is the quantity of heat (q) it absorbs or releases when it experiences a temperature change (ΔT) of 1 degree Celsius (or equivalently, 1 kelvin):

Equation:

$$C = \frac{q}{\Delta T}$$

Heat capacity is determined by both the type and amount of substance that absorbs or releases heat. It is therefore an extensive property—its value is proportional to the amount of the substance.

For example, consider the heat capacities of two cast iron frying pans. The heat capacity of the large pan is five times greater than that of the small pan because, although both are made of the same material, the mass of the large pan is five times greater than the mass of the small pan. More mass means more atoms are present in the larger pan, so it takes more energy to make all of those atoms vibrate faster. The heat capacity of the small cast iron frying pan is found by observing that it takes 18,150 J of energy to raise the temperature of the pan by 50.0 °C:

Equation:

$$C_{\text{small pan}} = \frac{18,140 \text{ J}}{50.0 \text{ }^{\circ}\text{C}} = 363 \text{ J/}^{\circ}\text{C}$$

The larger cast iron frying pan, while made of the same substance, requires 90,700 J of energy to raise its temperature by 50.0 °C. The larger pan has a

(proportionally) larger heat capacity because the larger amount of material requires a (proportionally) larger amount of energy to yield the same temperature change:

Equation:

$$C_{\text{large pan}} = \frac{90,700 \text{ J}}{50.0 \text{ }^{\circ}\text{C}} = 1814 \text{ J/}^{\circ}\text{C}$$

The **specific heat capacity (*c*)** of a substance, commonly called its “specific heat,” is the quantity of heat required to raise the temperature of 1 gram of a substance by 1 degree Celsius (or 1 kelvin):

Equation:

$$c = \frac{q}{m\Delta T}$$

Specific heat capacity depends only on the kind of substance absorbing or releasing heat. It is an intensive property—the type, but not the amount, of the substance is all that matters. For example, the small cast iron frying pan has a mass of 808 g. The specific heat of iron (the material used to make the pan) is therefore:

Equation:

$$c_{\text{iron}} = \frac{18,140 \text{ J}}{(808 \text{ g})(50.0 \text{ }^{\circ}\text{C})} = 0.449 \text{ J/g }^{\circ}\text{C}$$

The large frying pan has a mass of 4040 g. Using the data for this pan, we can also calculate the specific heat of iron:

Equation:

$$c_{\text{iron}} = \frac{90,700 \text{ J}}{(4040 \text{ g})(50.0 \text{ }^{\circ}\text{C})} = 0.449 \text{ J/g }^{\circ}\text{C}$$

Although the large pan is more massive than the small pan, since both are made of the same material, they both yield the same value for specific heat

(for the material of construction, iron). Note that specific heat is measured in units of energy per temperature per mass and is an intensive property, being derived from a ratio of two extensive properties (heat and mass). The molar heat capacity, also an intensive property, is the heat capacity per mole of a particular substance and has units of J/mol °C ([link](#)).



Due to its larger mass, a large frying pan has a larger heat capacity than a small frying pan. Because they are made of the same material, both frying pans have the same specific heat. (credit: Mark Blaser)

Liquid water has a relatively high specific heat (about 4.2 J/g °C); most metals have much lower specific heats (usually less than 1 J/g °C). The specific heat of a substance varies somewhat with temperature. However, this variation is usually small enough that we will treat specific heat as constant over the range of temperatures that will be considered in this chapter. Specific heats of some common substances are listed in [link](#).

Specific Heats of Common Substances at 25 °C and 1 bar		
Substance	Symbol (<i>state</i>)	Specific Heat (J/g °C)
helium	He(<i>g</i>)	5.193
water	H ₂ O(<i>l</i>)	4.184
ethanol	C ₂ H ₆ O(<i>l</i>)	2.376
ice	H ₂ O(<i>s</i>)	2.093 (at −10 °C)
water vapor	H ₂ O(<i>g</i>)	1.864
nitrogen	N ₂ (<i>g</i>)	1.040
air		1.007
oxygen	O ₂ (<i>g</i>)	0.918
aluminum	Al(<i>s</i>)	0.897
carbon dioxide	CO ₂ (<i>g</i>)	0.853
argon	Ar(<i>g</i>)	0.522
iron	Fe(<i>s</i>)	0.449
copper	Cu(<i>s</i>)	0.385
lead	Pb(<i>s</i>)	0.130
gold	Au(<i>s</i>)	0.129
silicon	Si(<i>s</i>)	0.712

If we know the mass of a substance and its specific heat, we can determine the amount of heat, q , entering or leaving the substance by measuring the temperature change before and after the heat is gained or lost:

Equation:

$$q = (\text{specific heat}) \times (\text{mass of substance}) \times (\text{temperature change})$$
$$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$$

In this equation, c is the specific heat of the substance, m is its mass, and ΔT (which is read “delta T”) is the temperature change, $T_{\text{final}} - T_{\text{initial}}$. If a substance gains thermal energy, its temperature increases, its final temperature is higher than its initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a positive value, and the value of q is positive. If a substance loses thermal energy, its temperature decreases, the final temperature is lower than the initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a negative value, and the value of q is negative.

Example:

Measuring Heat

A flask containing 8.0×10^2 g of water is heated, and the temperature of the water increases from 21 °C to 85 °C. How much heat did the water absorb?

Solution

To answer this question, consider these factors:

- the specific heat of the substance being heated (in this case, water)
- the amount of substance being heated (in this case, 8.0×10^2 g)
- the magnitude of the temperature change (in this case, from 21 °C to 85 °C).

The specific heat of water is 4.184 J/g °C, so to heat 1 g of water by 1 °C requires 4.184 J. We note that since 4.184 J is required to heat 1 g of water by 1 °C, we will need *800 times as much* to heat 8.0×10^2 g of water by 1 °C. Finally, we observe that since 4.184 J are required to heat 1 g of water

by 1 °C, we will need *64 times as much* to heat it by 64 °C (that is, from 21 °C to 85 °C).

This can be summarized using the equation:

Equation:

$$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$$

Equation:

$$\begin{aligned} &= (4.184 \text{ J/g } ^\circ\text{C}) \times (8.0 \times 10^2 \text{ g}) \times (85 - 21) ^\circ\text{C} \\ &= (4.184 \text{ J/g } ^\circ\text{C}) \times (8.0 \times 10^2 \text{ g}) \times (64) ^\circ\text{C} \\ &= 210,000 \text{ J } (= 2.1 \times 10^5 \text{ kJ}) \end{aligned}$$

Because the temperature increased, the water absorbed heat and q is positive.

Check Your Learning

How much heat, in joules, must be added to a $5.07 \times 10^4 \text{ g}$ iron skillet to increase its temperature from 25 °C to 250 °C? The specific heat of iron is 0.449 J/g °C.

Note:

Answer:

$$5.07 \times 10^4 \text{ J}$$

Note that the relationship between heat, specific heat, mass, and temperature change can be used to determine any of these quantities (not just heat) if the other three are known or can be deduced.

Example:**Determining Other Quantities**

A piece of unknown metal weighs 348 g. When the metal piece absorbs 6.64 kJ of heat, its temperature increases from 22.4 °C to 43.6 °C.

Determine the specific heat of this metal (which might provide a clue to its identity).

Solution

Since mass, heat, and temperature change are known for this metal, we can determine its specific heat using the relationship:

Equation:

$$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$$

Substituting the known values:

Equation:

$$6640 \text{ J} = c \times (348 \text{ g}) \times (43.6 - 22.4) ^\circ\text{C}$$

Solving:

Equation:

$$c = \frac{6640 \text{ J}}{(348 \text{ g}) \times (21.2 ^\circ\text{C})} = 0.900 \text{ J/g } ^\circ\text{C}$$

Comparing this value with the values in [\[link\]](#), this value matches the specific heat of aluminum, which suggests that the unknown metal may be aluminum.

Check Your Learning

A piece of unknown metal weighs 217 g. When the metal piece absorbs 1.43 kJ of heat, its temperature increases from 24.5 °C to 39.1 °C.

Determine the specific heat of this metal, and predict its identity.

Note:**Answer:**

$c = 0.451 \text{ J/g } ^\circ\text{C}$; the metal is likely to be iron

Note:

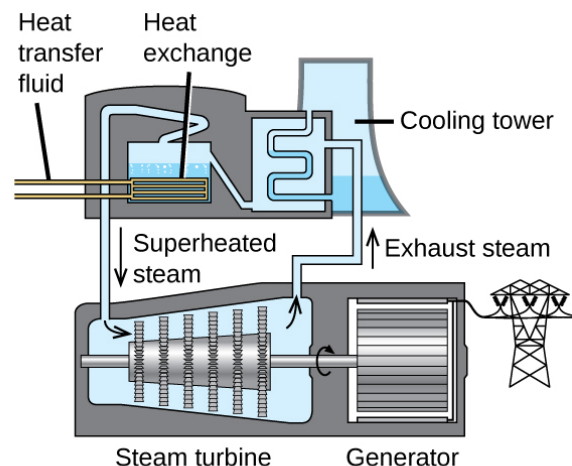
Solar Thermal Energy Power Plants

The sunlight that reaches the earth contains thousands of times more energy than we presently capture. Solar thermal systems provide one possible solution to the problem of converting energy from the sun into energy we can use. Large-scale solar thermal plants have different design specifics, but all concentrate sunlight to heat some substance; the heat “stored” in that substance is then converted into electricity.

The Solana Generating Station in Arizona’s Sonora Desert produces 280 megawatts of electrical power. It uses parabolic mirrors that focus sunlight on pipes filled with a heat transfer fluid (HTF) ([link](#)). The HTF then does two things: It turns water into steam, which spins turbines, which in turn produces electricity, and it melts and heats a mixture of salts, which functions as a thermal energy storage system. After the sun goes down, the molten salt mixture can then release enough of its stored heat to produce steam to run the turbines for 6 hours. Molten salts are used because they possess a number of beneficial properties, including high heat capacities and thermal conductivities.



(a)



(b)

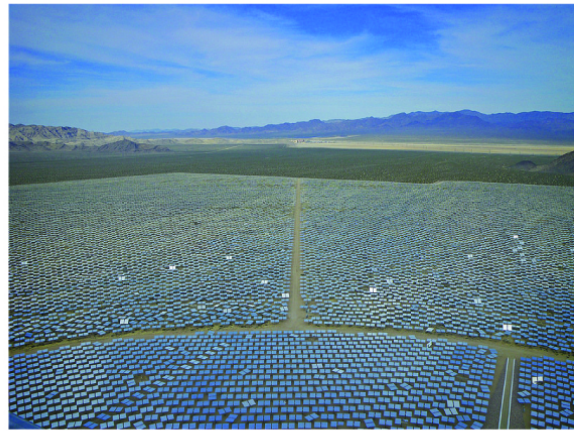
This solar thermal plant uses parabolic trough mirrors to concentrate sunlight. (credit a: modification of work by Bureau of Land

Management)

The 377-megawatt Ivanpah Solar Generating System, located in the Mojave Desert in California, is the largest solar thermal power plant in the world ([\[link\]](#)). Its 170,000 mirrors focus huge amounts of sunlight on three water-filled towers, producing steam at over 538 °C that drives electricity-producing turbines. It produces enough energy to power 140,000 homes. Water is used as the working fluid because of its large heat capacity and heat of vaporization.



(a)



(b)

(a) The Ivanpah solar thermal plant uses 170,000 mirrors to concentrate sunlight on water-filled towers. (b) It covers 4000 acres of public land near the Mojave Desert and the California-Nevada border.

(credit a: modification of work by Craig Dietrich; credit b: modification of work by “USFWS Pacific Southwest Region”/Flickr)

Key Concepts and Summary

Energy is the capacity to do work (applying a force to move matter). Kinetic energy (KE) is the energy of motion; potential energy is energy due to relative position, composition, or condition. When energy is converted

from one form into another, energy is neither created nor destroyed (law of conservation of energy or first law of thermodynamics).

Matter has thermal energy due to the KE of its molecules and temperature that corresponds to the average KE of its molecules. Heat is energy that is transferred between objects at different temperatures; it flows from a high to a low temperature. Chemical and physical processes can absorb heat (endothermic) or release heat (exothermic). The SI unit of energy, heat, and work is the joule (J).

Specific heat and heat capacity are measures of the energy needed to change the temperature of a substance or object. The amount of heat absorbed or released by a substance depends directly on the type of substance, its mass, and the temperature change it undergoes.

Key Equations

- $q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$

Chemistry End of Chapter Exercises

Exercise:

Problem:

A burning match and a bonfire may have the same temperature, yet you would not sit around a burning match on a fall evening to stay warm. Why not?

Solution:

The temperature of 1 gram of burning wood is approximately the same for both a match and a bonfire. This is an intensive property and depends on the material (wood). However, the overall amount of produced heat depends on the amount of material; this is an extensive property. The amount of wood in a bonfire is much greater than that in a match; the total amount of produced heat is also much greater, which

is why we can sit around a bonfire to stay warm, but a match would not provide enough heat to keep us from getting cold.

Exercise:

Problem:

Prepare a table identifying several energy transitions that take place during the typical operation of an automobile.

Exercise:

Problem:

Explain the difference between heat capacity and specific heat of a substance.

Solution:

Heat capacity refers to the heat required to raise the temperature of the mass of the substance 1 degree; specific heat refers to the heat required to raise the temperature of 1 gram of the substance 1 degree. Thus, heat capacity is an extensive property, and specific heat is an intensive one.

Exercise:

Problem:

Calculate the heat capacity, in joules and in calories per degree, of the following:

(a) 28.4 g of water

(b) 1.00 oz of lead

Exercise:

Problem:

Calculate the heat capacity, in joules and in calories per degree, of the following:

(a) 45.8 g of nitrogen gas

(b) 1.00 pound of aluminum metal

Solution:

(a) 47.6 J/°C; 11.38 cal °C⁻¹; (b) 407 J/°C; 97.3 cal °C⁻¹

Exercise:

Problem:

How much heat, in joules and in calories, must be added to a 75.0-g iron block with a specific heat of 0.449 J/g °C to increase its temperature from 25 °C to its melting temperature of 1535 °C?

Exercise:

Problem:

How much heat, in joules and in calories, is required to heat a 28.4-g (1-oz) ice cube from -23.0 °C to -1.0 °C?

Solution:

1310 J; 313 cal

Exercise:

Problem:

How much would the temperature of 275 g of water increase if 36.5 kJ of heat were added?

Exercise:

Problem:

If 14.5 kJ of heat were added to 485 g of liquid water, how much would its temperature increase?

Solution:

7.15 °C

Exercise:

Problem:

A piece of unknown substance weighs 44.7 g and requires 2110 J to increase its temperature from 23.2 °C to 89.6 °C.

- (a) What is the specific heat of the substance?
- (b) If it is one of the substances found in [\[link\]](#), what is its likely identity?

Exercise:

Problem:

A piece of unknown solid substance weighs 437.2 g, and requires 8460 J to increase its temperature from 19.3 °C to 68.9 °C.

- (a) What is the specific heat of the substance?
- (b) If it is one of the substances found in [\[link\]](#), what is its likely identity?

Solution:

- (a) 0.390 J/g °C; (b) Copper is a likely candidate.

Exercise:

Problem: An aluminum kettle weighs 1.05 kg.

- (a) What is the heat capacity of the kettle?
- (b) How much heat is required to increase the temperature of this kettle from 23.0 °C to 99.0 °C?
- (c) How much heat is required to heat this kettle from 23.0 °C to 99.0 °C if it contains 1.25 L of water (density of 0.997 g/mL and a specific

heat of 4.184 J/g °C)?

Exercise:

Problem:

Most people find waterbeds uncomfortable unless the water temperature is maintained at about 85 °F. Unless it is heated, a waterbed that contains 892 L of water cools from 85 °F to 72 °F in 24 hours. Estimate the amount of electrical energy required over 24 hours, in kWh, to keep the bed from cooling. Note that 1 kilowatt-hour (kWh) = 3.6×10^6 J, and assume that the density of water is 1.0 g/mL (independent of temperature). What other assumptions did you make? How did they affect your calculated result (i.e., were they likely to yield “positive” or “negative” errors)?

Solution:

We assume that the density of water is 1.0 g/cm³(1 g/mL) and that it takes as much energy to keep the water at 85 °F as to heat it from 72 °F to 85 °F. We also assume that only the water is going to be heated.
Energy required = 7.47 kWh

Glossary

calorie (cal)

unit of heat or other energy; the amount of energy required to raise 1 gram of water by 1 degree Celsius; 1 cal is defined as 4.184 J

endothermic process

chemical reaction or physical change that absorbs heat

energy

capacity to supply heat or do work

exothermic process

chemical reaction or physical change that releases heat

heat (q)

transfer of thermal energy between two bodies

heat capacity (C)

extensive property of a body of matter that represents the quantity of heat required to increase its temperature by 1 degree Celsius (or 1 kelvin)

joule (J)

SI unit of energy; 1 joule is the kinetic energy of an object with a mass of 2 kilograms moving with a velocity of 1 meter per second, $1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2$ and $4.184 \text{ J} = 1 \text{ cal}$

kinetic energy

energy of a moving body, in joules, equal to $\frac{1}{2}mv^2$ (where m = mass and v = velocity)

potential energy

energy of a particle or system of particles derived from relative position, composition, or condition

specific heat capacity (c)

intensive property of a substance that represents the quantity of heat required to raise the temperature of 1 gram of the substance by 1 degree Celsius (or 1 kelvin)

temperature

intensive property of matter that is a quantitative measure of “hotness” and “coldness”

thermal energy

kinetic energy associated with the random motion of atoms and molecules

thermochemistry

study of measuring the amount of heat absorbed or released during a chemical reaction or a physical change

work (w)

energy transfer due to changes in external, macroscopic variables such as pressure and volume; or causing matter to move against an opposing force

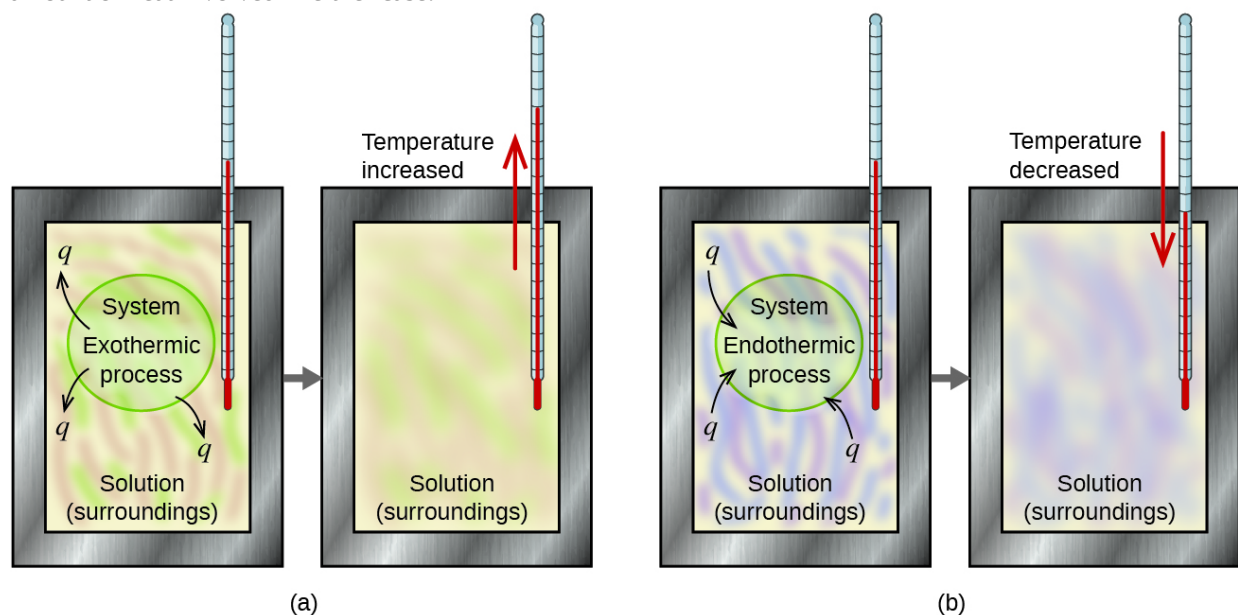
Calorimetry

By the end of this section, you will be able to:

- Explain the technique of calorimetry
- Calculate and interpret heat and related properties using typical calorimetry data

One technique we can use to measure the amount of heat involved in a chemical or physical process is known as **calorimetry**. Calorimetry is used to measure amounts of heat transferred to or from a substance. To do so, the heat is exchanged with a calibrated object (calorimeter). The temperature change measured by the calorimeter is used to derive the amount of heat transferred by the process under study. The measurement of heat transfer using this approach requires the definition of a **system** (the substance or substances undergoing the chemical or physical change) and its **surroundings** (the other components of the measurement apparatus that serve to either provide heat to the system or absorb heat from the system). Knowledge of the heat capacity of the surroundings, and careful measurements of the masses of the system and surroundings and their temperatures before and after the process allows one to calculate the heat transferred as described in this section.

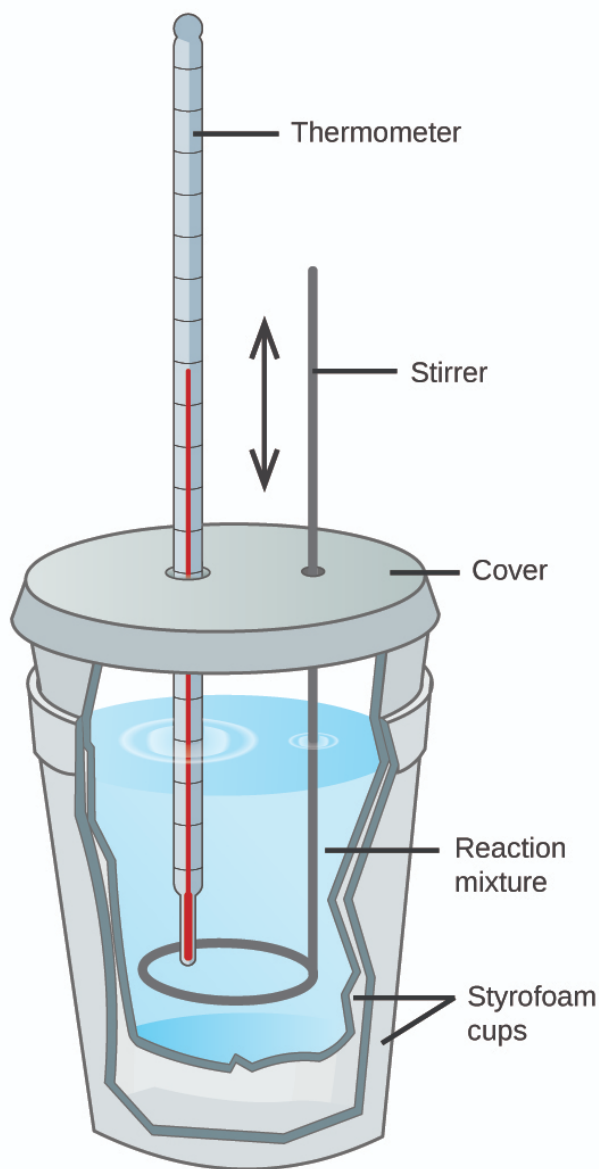
A **calorimeter** is a device used to measure the amount of heat involved in a chemical or physical process. For example, when an exothermic reaction occurs in solution in a calorimeter, the heat produced by the reaction is absorbed by the solution, which increases its temperature. When an endothermic reaction occurs, the heat required is absorbed from the thermal energy of the solution, which decreases its temperature ([link](#)). The temperature change, along with the specific heat and mass of the solution, can then be used to calculate the amount of heat involved in either case.



In a calorimetric determination, either (a) an exothermic process occurs and heat, q , is negative, indicating that thermal energy is transferred from the system to its surroundings, or (b) an endothermic process occurs and heat, q , is positive, indicating that thermal energy is transferred from the surroundings to the system.

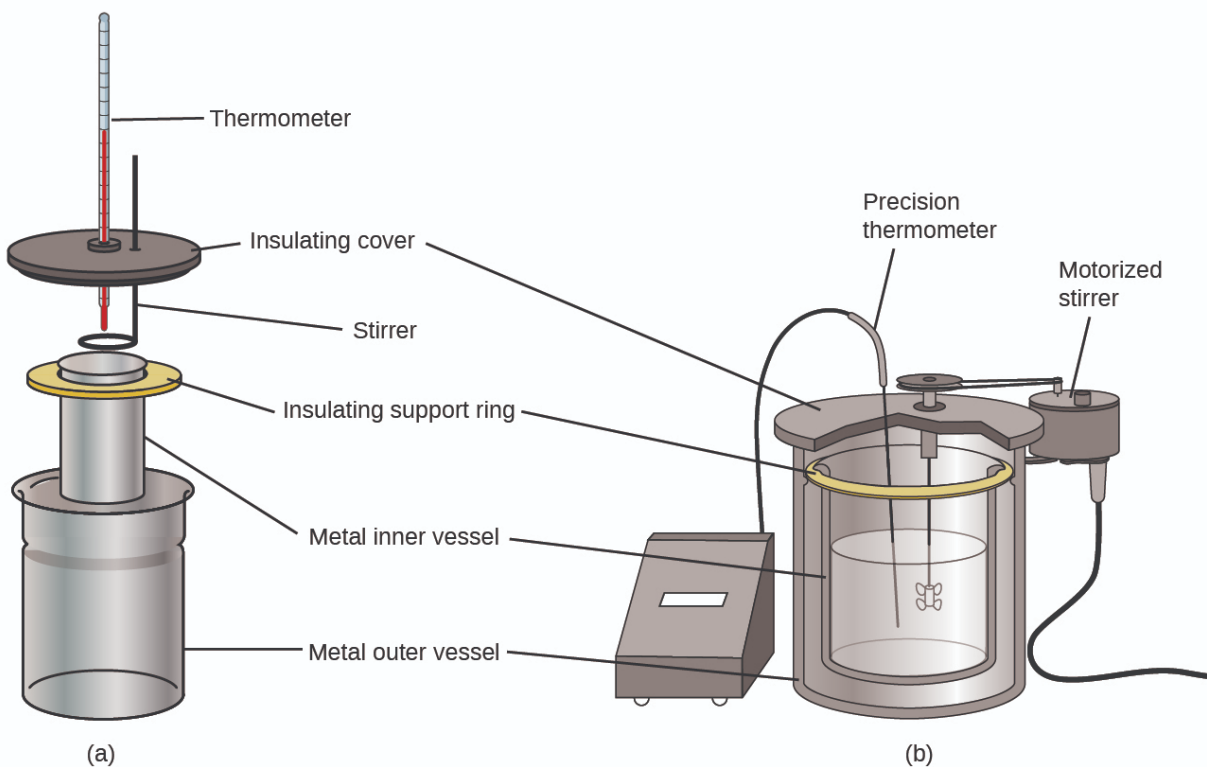
Scientists use well-insulated calorimeters that all but prevent the transfer of heat between the calorimeter and its environment. This enables the accurate determination of the heat involved in chemical processes, the energy content of foods, and so on. General chemistry students often use simple calorimeters constructed from

polystyrene cups ([link](#)). These easy-to-use “coffee cup” calorimeters allow more heat exchange with the outside environment, and therefore produce less accurate energy values.



A simple calorimeter can be constructed from two polystyrene cups. A thermometer and stirrer extend through the cover into the reaction mixture.

Commercial solution calorimeters are also available. Relatively inexpensive calorimeters often consist of two thin-walled cups that are nested in a way that minimizes thermal contact during use, along with an insulated cover, handheld stirrer, and simple thermometer. More expensive calorimeters used for industry and research typically have a well-insulated, fully enclosed reaction vessel, motorized stirring mechanism, and a more accurate temperature sensor ([link](#)).



Commercial solution calorimeters range from (a) simple, inexpensive models for student use to (b) expensive, more accurate models for industry and research.

Before we practice calorimetry problems involving chemical reactions, consider a simpler example that illustrates the core idea behind calorimetry. Suppose we initially have a high-temperature substance, such as a hot piece of metal (M), and a low-temperature substance, such as cool water (W). If we place the metal in the water, heat will flow from M to W. The temperature of M will decrease, and the temperature of W will increase, until the two substances have the same temperature—that is, when they reach thermal equilibrium ([Link](#)). If this occurs in a calorimeter, ideally all of this heat transfer occurs between the two substances, with no heat gained or lost by either the calorimeter or the calorimeter's surroundings. Under these ideal circumstances, the net heat change is zero:

Equation:

$$q_{\text{substance M}} + q_{\text{substance W}} = 0$$

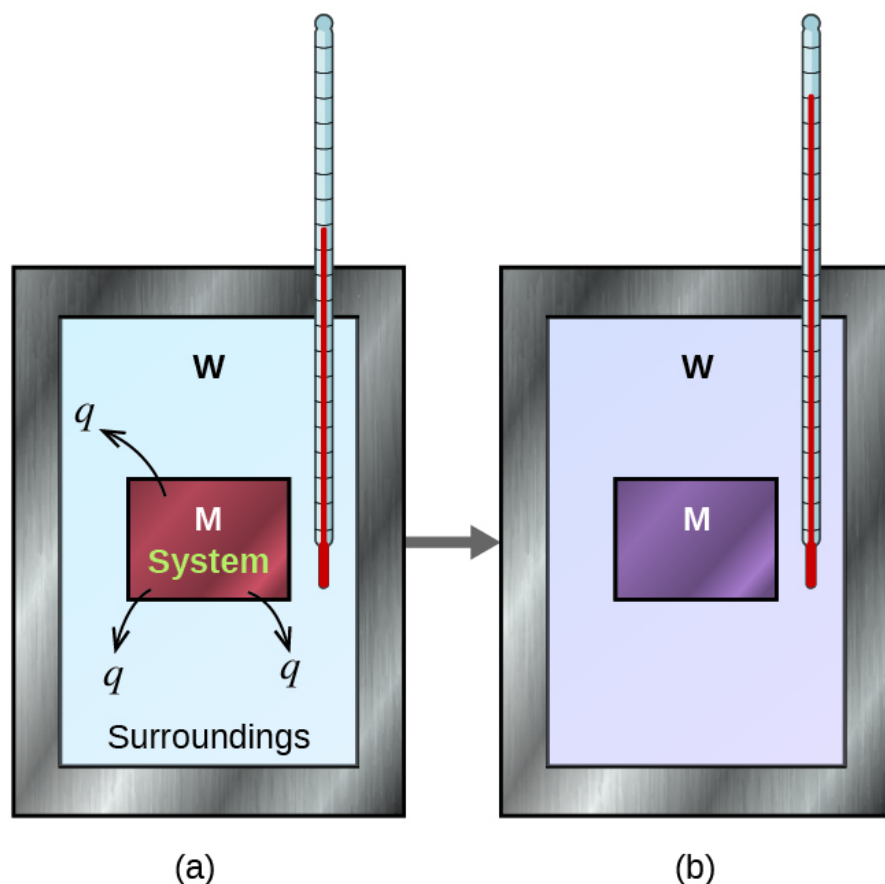
This relationship can be rearranged to show that the heat gained by substance M is equal to the heat lost by substance W:

Equation:

$$q_{\text{substance M}} = -q_{\text{substance W}}$$

The magnitude of the heat (change) is therefore the same for both substances, and the negative sign merely shows that $q_{\text{substance M}}$ and $q_{\text{substance W}}$ are opposite in direction of heat flow (gain or loss) but does not indicate the arithmetic sign of either q value (that is determined by whether the matter in question gains or loses heat,

per definition). In the specific situation described, $q_{\text{substance M}}$ is a negative value and $q_{\text{substance W}}$ is positive, since heat is transferred from M to W.



In a simple calorimetry process, (a) heat, q , is transferred from the hot metal, M, to the cool water, W, until (b) both are at the same temperature.

Example:

Heat Transfer between Substances at Different Temperatures

A 360.0-g piece of rebar (a steel rod used for reinforcing concrete) is dropped into 425 mL of water at 24.0 °C. The final temperature of the water was measured as 42.7 °C. Calculate the initial temperature of the piece of rebar. Assume the specific heat of steel is approximately the same as that for iron ([link](#)), and that all heat transfer occurs between the rebar and the water (there is no heat exchange with the surroundings).

Solution

The temperature of the water increases from 24.0 °C to 42.7 °C, so the water absorbs heat. That heat came from the piece of rebar, which initially was at a higher temperature. Assuming that all heat transfer was between the rebar and the water, with no heat “lost” to the outside environment, then *heat given off by rebar* = *–heat taken in by water*, or:

Equation:

$$q_{\text{rebar}} = -q_{\text{water}}$$

Since we know how heat is related to other measurable quantities, we have:

Equation:

$$(c \times m \times \Delta T)_{\text{rebar}} = -(c \times m \times \Delta T)_{\text{water}}$$

Letting f = final and i = initial, in expanded form, this becomes:

Equation:

$$c_{\text{rebar}} \times m_{\text{rebar}} \times (T_{\text{f, rebar}} - T_{\text{i, rebar}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f, water}} - T_{\text{i, water}})$$

The density of water is 1.0 g/mL, so 425 mL of water = 425 g. Noting that the final temperature of both the rebar and water is 42.7 °C, substituting known values yields:

Equation:

$$(0.449 \text{ J/g } ^\circ\text{C})(360.0 \text{ g})(42.7 ^\circ\text{C} - T_{\text{i, rebar}}) = -(4.184 \text{ J/g } ^\circ\text{C})(425 \text{ g})(42.7 ^\circ\text{C} - 24.0 ^\circ\text{C})$$

Equation:

$$T_{\text{i, rebar}} = \frac{(4.184 \text{ J/g } ^\circ\text{C})(425 \text{ g})(42.7 ^\circ\text{C} - 24.0 ^\circ\text{C})}{(0.449 \text{ J/g } ^\circ\text{C})(360.0 \text{ g})} + 42.7 ^\circ\text{C}$$

Solving this gives $T_{\text{i, rebar}} = 248 ^\circ\text{C}$, so the initial temperature of the rebar was 248 °C.

Check Your Learning

A 248-g piece of copper is dropped into 390 mL of water at 22.6 °C. The final temperature of the water was measured as 39.9 °C. Calculate the initial temperature of the piece of copper. Assume that all heat transfer occurs between the copper and the water.

Note:

Answer:

The initial temperature of the copper was 335.6 °C.

Check Your Learning

A 248-g piece of copper initially at 314 °C is dropped into 390 mL of water initially at 22.6 °C. Assuming that all heat transfer occurs between the copper and the water, calculate the final temperature.

Note:

Answer:

The final temperature (reached by both copper and water) is 38.7 °C.

This method can also be used to determine other quantities, such as the specific heat of an unknown metal.

Example:

Identifying a Metal by Measuring Specific Heat

A 59.7 g piece of metal that had been submerged in boiling water was quickly transferred into 60.0 mL of water initially at 22.0 °C. The final temperature is 28.5 °C. Use these data to determine the specific heat of the metal. Use this result to identify the metal.

Solution

Assuming perfect heat transfer, *heat given off by metal* = *−heat taken in by water*, or:

Equation:

$$q_{\text{metal}} = -q_{\text{water}}$$

In expanded form, this is:

Equation:

$$c_{\text{metal}} \times m_{\text{metal}} \times (T_{\text{f,metal}} - T_{\text{i,metal}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f,water}} - T_{\text{i,water}})$$

Noting that since the metal was submerged in boiling water, its initial temperature was 100.0 °C; and that for water, 60.0 mL = 60.0 g; we have:

Equation:

$$(c_{\text{metal}})(59.7 \text{ g})(28.5 \text{ }^{\circ}\text{C} - 100.0 \text{ }^{\circ}\text{C}) = -(4.18 \text{ J/g }^{\circ}\text{C})(60.0 \text{ g})(28.5 \text{ }^{\circ}\text{C} - 22.0 \text{ }^{\circ}\text{C})$$

Solving this:

Equation:

$$c_{\text{metal}} = \frac{-(4.184 \text{ J/g }^{\circ}\text{C})(60.0 \text{ g})(6.5 \text{ }^{\circ}\text{C})}{(59.7 \text{ g})(-71.5 \text{ }^{\circ}\text{C})} = 0.38 \text{ J/g }^{\circ}\text{C}$$

Comparing this with values in [\[link\]](#), our experimental specific heat is closest to the value for copper (0.39 J/g °C), so we identify the metal as copper.

Check Your Learning

A 92.9-g piece of a silver/gray metal is heated to 178.0 °C, and then quickly transferred into 75.0 mL of water initially at 24.0 °C. After 5 minutes, both the metal and the water have reached the same temperature: 29.7 °C. Determine the specific heat and the identity of the metal. (Note: You should find that the specific heat is close to that of two different metals. Explain how you can confidently determine the identity of the metal).

Note:

Answer:

$$c_{\text{metal}} = 0.13 \text{ J/g }^{\circ}\text{C}$$

This specific heat is close to that of either gold or lead. It would be difficult to determine which metal this was based solely on the numerical values. However, the observation that the metal is silver/gray in addition to the value for the specific heat indicates that the metal is lead.

When we use calorimetry to determine the heat involved in a chemical reaction, the same principles we have been discussing apply. The amount of heat absorbed by the calorimeter is often small enough that we can neglect it (though not for highly accurate measurements, as discussed later), and the calorimeter minimizes energy exchange with the outside environment. Because energy is neither created nor destroyed during a chemical reaction, there is no overall energy change during the reaction. The heat produced or consumed in the reaction (the “system”), q_{reaction} , plus the heat absorbed or lost by the solution (the “surroundings”), q_{solution} , must add up to zero:

Equation:

$$q_{\text{reaction}} + q_{\text{solution}} = 0$$

This means that the amount of heat produced or consumed in the reaction equals the amount of heat absorbed or lost by the solution:

Equation:

$$q_{\text{reaction}} = -q_{\text{solution}}$$

This concept lies at the heart of all calorimetry problems and calculations.

Example:

Heat Produced by an Exothermic Reaction

When 50.0 mL of 1.00 M HCl(aq) and 50.0 mL of 1.00 M NaOH(aq), both at 22.0 °C, are added to a coffee cup calorimeter, the temperature of the mixture reaches a maximum of 28.9 °C. What is the approximate amount of heat produced by this reaction?

Equation:



Solution

To visualize what is going on, imagine that you could combine the two solutions so quickly that no reaction took place while they mixed; then after mixing, the reaction took place. At the instant of mixing, you have 100.0 mL of a mixture of HCl and NaOH at 22.0 °C. The HCl and NaOH then react until the solution temperature reaches 28.9 °C.

The heat given off by the reaction is equal to that taken in by the solution. Therefore:

Equation:

$$q_{\text{reaction}} = -q_{\text{solution}}$$

(It is important to remember that this relationship only holds if the calorimeter does not absorb any heat from the reaction, and there is no heat exchange between the calorimeter and the outside environment.)

Next, we know that the heat absorbed by the solution depends on its specific heat, mass, and temperature change:

Equation:

$$q_{\text{solution}} = (c \times m \times \Delta T)_{\text{solution}}$$

To proceed with this calculation, we need to make a few more reasonable assumptions or approximations.

Since the solution is aqueous, we can proceed as if it were water in terms of its specific heat and mass values.

The density of water is approximately 1.0 g/mL, so 100.0 mL has a mass of about 1.0×10^2 g (two significant figures). The specific heat of water is approximately 4.184 J/g °C, so we use that for the specific heat of the solution. Substituting these values gives:

Equation:

$$q_{\text{solution}} = (4.184 \text{ J/g } ^\circ\text{C})(1.0 \times 10^2 \text{ g})(28.9 ^\circ\text{C} - 22.0 ^\circ\text{C}) = 2.9 \times 10^3 \text{ J}$$

Finally, since we are trying to find the heat of the reaction, we have:

Equation:

$$q_{\text{reaction}} = -q_{\text{solution}} = -2.9 \times 10^3 \text{ J}$$

The negative sign indicates that the reaction is exothermic. It produces 2.9 kJ of heat.

Check Your Learning

When 100 mL of 0.200 M NaCl(aq) and 100 mL of 0.200 M AgNO₃(aq), both at 21.9 °C, are mixed in a coffee cup calorimeter, the temperature increases to 23.5 °C as solid AgCl forms. How much heat is produced by this precipitation reaction? What assumptions did you make to determine your value?

Note:

Answer:

$1.34 \times 10^3 \text{ J}$; assume no heat is absorbed by the calorimeter, no heat is exchanged between the calorimeter and its surroundings, and that the specific heat and mass of the solution are the same as those for water

Note:

Thermochemistry of Hand Warmers

When working or playing outdoors on a cold day, you might use a hand warmer to warm your hands ([link](#)). A common reusable hand warmer contains a supersaturated solution of $\text{NaC}_2\text{H}_3\text{O}_2$ (sodium acetate) and a metal disc. Bending the disk creates nucleation sites around which the metastable $\text{NaC}_2\text{H}_3\text{O}_2$ quickly crystallizes (a later chapter on solutions will investigate saturation and supersaturation in more detail).

The process $\text{NaC}_2\text{H}_3\text{O}_2(aq) \rightarrow \text{NaC}_2\text{H}_3\text{O}_2(s)$ is exothermic, and the heat produced by this process is absorbed by your hands, thereby warming them (at least for a while). If the hand warmer is reheated, the $\text{NaC}_2\text{H}_3\text{O}_2$ redissolves and can be reused.



Chemical hand warmers produce heat that warms your hand on a cold day. In this one, you can see the metal disc that initiates the exothermic precipitation reaction. (credit: modification of work by Science Buddies TV/YouTube)

Another common hand warmer produces heat when it is ripped open, exposing iron and water in the hand warmer to oxygen in the air. One simplified version of this exothermic reaction is $2\text{Fe}(s) + \frac{3}{2}\text{O}_2(g) \rightarrow \text{Fe}_2\text{O}_3(s)$. Salt in the hand warmer catalyzes the reaction, so it produces heat more rapidly; cellulose, vermiculite, and activated carbon help distribute the heat evenly. Other types of hand warmers use lighter fluid (a platinum catalyst helps lighter fluid oxidize exothermically), charcoal (charcoal oxidizes in a special case), or electrical units that produce heat by passing an electrical current from a battery through resistive wires.

Note:



This [link](#) shows the precipitation reaction that occurs when the disk in a chemical hand warmer is flexed.

Example:**Heat Flow in an Instant Ice Pack**

When solid ammonium nitrate dissolves in water, the solution becomes cold. This is the basis for an “instant ice pack” ([link](#)). When 3.21 g of solid NH_4NO_3 dissolves in 50.0 g of water at 24.9 °C in a calorimeter, the temperature decreases to 20.3 °C.

Calculate the value of q for this reaction and explain the meaning of its arithmetic sign. State any assumptions that you made.



An instant cold pack consists of a bag containing solid ammonium nitrate and a second bag of water. When the bag of water is broken, the pack becomes cold because the dissolution of ammonium nitrate is an endothermic process that removes thermal energy from the water. The cold pack then removes thermal energy from your body.

Solution

We assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself), in which case:

Equation:

$$q_{\text{rxn}} = -q_{\text{soln}}$$

with “rxn” and “soln” used as shorthand for “reaction” and “solution,” respectively.

Assuming also that the specific heat of the solution is the same as that for water, we have:

Equation:

$$\begin{aligned}q_{\text{rxn}} &= -q_{\text{soln}} = -(c \times m \times \Delta T)_{\text{soln}} \\&= -[(4.184 \text{ J/g } ^\circ\text{C}) \times (53.2 \text{ g}) \times (20.3 ^\circ\text{C} - 24.9 ^\circ\text{C})] \\&= -[(4.184 \text{ J/g } ^\circ\text{C}) \times (53.2 \text{ g}) \times (-4.6 ^\circ\text{C})] \\&+1.0 \times 10^3 \text{ J} = +1.0 \text{ kJ}\end{aligned}$$

The positive sign for q indicates that the dissolution is an endothermic process.

Check Your Learning

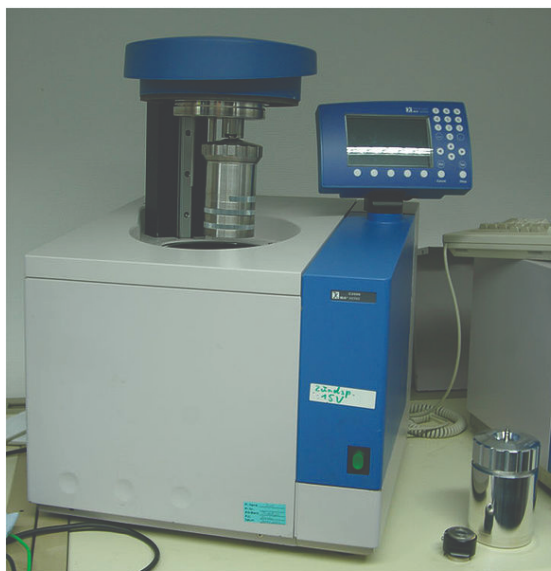
When a 3.00-g sample of KCl was added to 3.00×10^2 g of water in a coffee cup calorimeter, the temperature decreased by 1.05 °C. How much heat is involved in the dissolution of the KCl? What assumptions did you make?

Note:**Answer:**

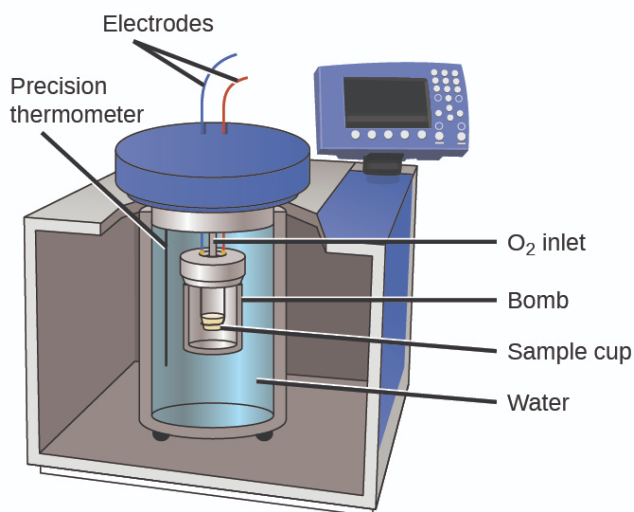
1.33 kJ; assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself) and that the specific heat of the solution is the same as that for water

If the amount of heat absorbed by a calorimeter is too large to neglect or if we require more accurate results, then we must take into account the heat absorbed both by the solution and by the calorimeter.

The calorimeters described are designed to operate at constant (atmospheric) pressure and are convenient to measure heat flow accompanying processes that occur in solution. A different type of calorimeter that operates at constant volume, colloquially known as a **bomb calorimeter**, is used to measure the energy produced by reactions that yield large amounts of heat and gaseous products, such as combustion reactions. (The term “bomb” comes from the observation that these reactions can be vigorous enough to resemble explosions that would damage other calorimeters.) This type of calorimeter consists of a robust steel container (the “bomb”) that contains the reactants and is itself submerged in water ([link](#)). The sample is placed in the bomb, which is then filled with oxygen at high pressure. A small electrical spark is used to ignite the sample. The energy produced by the reaction is absorbed by the steel bomb and the surrounding water. The temperature increase is measured and, along with the known heat capacity of the calorimeter, is used to calculate the energy produced by the reaction. Bomb calorimeters require calibration to determine the heat capacity of the calorimeter and ensure accurate results. The calibration is accomplished using a reaction with a known q , such as a measured quantity of benzoic acid ignited by a spark from a nickel fuse wire that is weighed before and after the reaction. The temperature change produced by the known reaction is used to determine the heat capacity of the calorimeter. The calibration is generally performed each time before the calorimeter is used to gather research data.



(a)



(b)

(a) A bomb calorimeter is used to measure heat produced by reactions involving gaseous reactants or products, such as combustion. (b) The reactants are contained in the gas-tight “bomb,” which is submerged in water and surrounded by insulating materials. (credit a: modification of work by “Harbor1”/Wikimedia commons)

Note:



Click on this [link](#) to view how a bomb calorimeter is prepared for action. This [site](#) shows calorimetric calculations using sample data.

Example:

Bomb Calorimetry

When 3.12 g of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, is burned in a bomb calorimeter, the temperature of the calorimeter increases from 23.8 °C to 35.6 °C. The calorimeter contains 775 g of water, and the bomb itself has a heat capacity of 893 J/°C. How much heat was produced by the combustion of the glucose sample?

Solution

The combustion produces heat that is primarily absorbed by the water and the bomb. (The amounts of heat absorbed by the reaction products and the unreacted excess oxygen are relatively small and dealing with them is beyond the scope of this text. We will neglect them in our calculations.)

The heat produced by the reaction is absorbed by the water and the bomb:

Equation:

$$\begin{aligned}
 q_{\text{rxn}} &= -(q_{\text{water}} + q_{\text{bomb}}) \\
 &= -[(4.184 \text{ J/g } ^\circ\text{C}) \times (775 \text{ g}) \times (35.6 ^\circ\text{C} - 23.8 ^\circ\text{C}) + 893 \text{ J/}^\circ\text{C} \times (35.6 ^\circ\text{C} - 23.8 ^\circ\text{C})] \\
 &= -(38,300 \text{ J} + 10,500 \text{ J}) \\
 &= -48,800 \text{ J} = -48.8 \text{ kJ}
 \end{aligned}$$

This reaction released 48.7 kJ of heat when 3.12 g of glucose was burned.

Check Your Learning

When 0.963 g of benzene, C_6H_6 , is burned in a bomb calorimeter, the temperature of the calorimeter increases by $8.39 ^\circ\text{C}$. The bomb has a heat capacity of $784 \text{ J/}^\circ\text{C}$ and is submerged in 925 mL of water. How much heat was produced by the combustion of the glucose sample?

Note:

Answer:

39.0 kJ

Since the first one was constructed in 1899, 35 calorimeters have been built to measure the heat produced by a living person.^[footnote] These whole-body calorimeters of various designs are large enough to hold an individual human being. More recently, whole-room calorimeters allow for relatively normal activities to be performed, and these calorimeters generate data that more closely reflect the real world. These calorimeters are used to measure the metabolism of individuals under different environmental conditions, different dietary regimes, and with different health conditions, such as diabetes. In humans, metabolism is typically measured in Calories per day. A **nutritional calorie (Calorie)** is the energy unit used to quantify the amount of energy derived from the metabolism of foods; one Calorie is equal to 1000 calories (1 kcal), the amount of energy needed to heat 1 kg of water by $1 ^\circ\text{C}$.

Francis D. Reardon et al. "The Snellen human calorimeter revisited, re-engineered and upgraded: Design and performance characteristics." *Medical and Biological Engineering and Computing* 8 (2006)721–28, <http://link.springer.com/article/10.1007/s11517-006-0086-5>.

Note:

Measuring Nutritional Calories

In your day-to-day life, you may be more familiar with energy being given in Calories, or nutritional calories, which are used to quantify the amount of energy in foods. One calorie (cal) = exactly 4.184 joules, and one Calorie (note the capitalization) = 1000 cal, or 1 kcal. (This is approximately the amount of energy needed to heat 1 kg of water by $1 ^\circ\text{C}$.)

The macronutrients in food are proteins, carbohydrates, and fats or oils. Proteins provide about 4 Calories per gram, carbohydrates also provide about 4 Calories per gram, and fats and oils provide about 9 Calories/g. Nutritional labels on food packages show the caloric content of one serving of the food, as well as the breakdown into Calories from each of the three macronutrients ([link](#)).



(a)

Sample label for macaroni & cheese

Nutrition Facts	
① Start here	Serving Size 1 cup (228g) Servings Per Container 2
② Check Calories	Amount Per Serving Calories 250 Calories from Fat 110
③ Limit these nutrients	% Daily Value*
	Total Fat 12g 18%
	Saturated Fat 3g 15%
	Trans Fat 3g
	Cholesterol 30mg 10%
	Sodium 470mg 20%
	Total Carbohydrates 31g 10%
	Dietary Fiber 0g 0%
	Sugars 5g
	Protein 5g
④ Get enough of these nutrients	Vitamin A 4%
	Vitamin C 2%
	Calcium 20%
	Iron 4%
⑤ Footnote	*Percent Daily Values are based on a 2,000 calorie diet. Your Daily Values may be higher or lower depending on your calorie needs.
	Calories 2,000 2,500
	Total Fat Less than 65g 80g
	Sat Fat Less than 20g 25g
	Cholesterol Less than 300mg 300mg
	Sodium Less than 2,400mg 2,400mg
	Total Carbohydrate 300g 375g
	Dietary Fiber 25g 30g

⑥ Quick guide to % DV
• 5% or less is low
• 20% or more is high

(b)

(a) Macaroni and cheese contain energy in the form of the macronutrients in the food. (b) The food's nutritional information is shown on the package label. In the US, the energy content is given in Calories (per serving); the rest of the world usually uses kilojoules. (credit a: modification of work by "Rex Roof"/Flickr)

For the example shown in (b), the total energy per 228-g portion is calculated by:

Equation:

$$(5 \text{ g protein} \times 4 \text{ Calories/g}) + (31 \text{ g carb} \times 4 \text{ Calories/g}) + (12 \text{ g fat} \times 9 \text{ Calories/g}) = 252 \text{ Calories}$$

So, you can use food labels to count your Calories. But where do the values come from? And how accurate are they? The caloric content of foods can be determined by using bomb calorimetry; that is, by burning the food and measuring the energy it contains. A sample of food is weighed, mixed in a blender, freeze-dried, ground into powder, and formed into a pellet. The pellet is burned inside a bomb calorimeter, and the measured temperature change is converted into energy per gram of food.

Today, the caloric content on food labels is derived using a method called the Atwater system that uses the average caloric content of the different chemical constituents of food, protein, carbohydrate, and fats. The average amounts are those given in the equation and are derived from the various results given by bomb calorimetry of whole foods. The carbohydrate amount is discounted a certain amount for the fiber content, which is indigestible carbohydrate. To determine the energy content of a food, the quantities of carbohydrate, protein, and fat are each multiplied by the average Calories per gram for each and the products summed to obtain the total energy.

Note:



Click on this [link](#) to access the US Department of Agriculture (USDA) National Nutrient Database, containing nutritional information on over 8000 foods.

Key Concepts and Summary

Calorimetry is used to measure the amount of thermal energy transferred in a chemical or physical process. This requires careful measurement of the temperature change that occurs during the process and the masses of the system and surroundings. These measured quantities are then used to compute the amount of heat produced or consumed in the process using known mathematical relations.

Calorimeters are designed to minimize energy exchange between the system being studied and its surroundings. They range from simple coffee cup calorimeters used by introductory chemistry students to sophisticated bomb calorimeters used to determine the energy content of food.

Chemistry End of Chapter Exercises

Exercise:

Problem:

A 500-mL bottle of water at room temperature and a 2-L bottle of water at the same temperature were placed in a refrigerator. After 30 minutes, the 500-mL bottle of water had cooled to the temperature of the refrigerator. An hour later, the 2-L of water had cooled to the same temperature. When asked which sample of water lost the most heat, one student replied that both bottles lost the same amount of heat because they started at the same temperature and finished at the same temperature. A second student thought that the 2-L bottle of water lost more heat because there was more water. A third student believed that the 500-mL bottle of water lost more heat because it cooled more quickly. A fourth student thought that it was not possible to tell because we do not know the initial temperature and the final temperature of the water. Indicate which of these answers is correct and describe the error in each of the other answers.

Exercise:

Problem:

Would the amount of heat measured for the reaction in [\[link\]](#) be greater, lesser, or remain the same if we used a calorimeter that was a poorer insulator than a coffee cup calorimeter? Explain your answer.

Solution:

lesser; more heat would be lost to the coffee cup and the environment and so ΔT for the water would be lesser and the calculated q would be lesser

Exercise:

Problem:

Would the amount of heat absorbed by the dissolution in [\[link\]](#) appear greater, lesser, or remain the same if the experimenter used a calorimeter that was a poorer insulator than a coffee cup calorimeter? Explain your answer.

Exercise:**Problem:**

Would the amount of heat absorbed by the dissolution in [\[link\]](#) appear greater, lesser, or remain the same if the heat capacity of the calorimeter were taken into account? Explain your answer.

Solution:

greater, since taking the calorimeter's heat capacity into account will compensate for the thermal energy transferred to the solution from the calorimeter; this approach includes the calorimeter itself, along with the solution, as "surroundings": $q_{\text{rxn}} = -(q_{\text{solution}} + q_{\text{calorimeter}})$; since both q_{solution} and $q_{\text{calorimeter}}$ are negative, including the latter term (q_{rxn}) will yield a greater value for the heat of the dissolution

Exercise:**Problem:**

How many milliliters of water at 23 °C with a density of 1.00 g/mL must be mixed with 180 mL (about 6 oz) of coffee at 95 °C so that the resulting combination will have a temperature of 60 °C? Assume that coffee and water have the same density and the same specific heat.

Exercise:**Problem:**

How much will the temperature of a cup (180 g) of coffee at 95 °C be reduced when a 45 g silver spoon (specific heat 0.24 J/g °C) at 25 °C is placed in the coffee and the two are allowed to reach the same temperature? Assume that the coffee has the same density and specific heat as water.

Solution:

The temperature of the coffee will drop 1 degree.

Exercise:**Problem:**

A 45-g aluminum spoon (specific heat 0.88 J/g °C) at 24 °C is placed in 180 mL (180 g) of coffee at 85 °C and the temperature of the two become equal.

(a) What is the final temperature when the two become equal? Assume that coffee has the same specific heat as water.

(b) The first time a student solved this problem she got an answer of 88 °C. Explain why this is clearly an incorrect answer.

Exercise:**Problem:**

The temperature of the cooling water as it leaves the hot engine of an automobile is 240 °F. After it passes through the radiator it has a temperature of 175 °F. Calculate the amount of heat transferred from the engine to the surroundings by one gallon of water with a specific heat of 4.184 J/g °C.

Solution:

$5.7 \times 10^2 \text{ kJ}$

Exercise:

Problem:

A 70.0-g piece of metal at 80.0 °C is placed in 100 g of water at 22.0 °C contained in a calorimeter like that shown in [\[link\]](#). The metal and water come to the same temperature at 24.6 °C. How much heat did the metal give up to the water? What is the specific heat of the metal?

Exercise:**Problem:**

If a reaction produces 1.506 kJ of heat, which is trapped in 30.0 g of water initially at 26.5 °C in a calorimeter like that in [\[link\]](#), what is the resulting temperature of the water?

Solution:

38.5 °C

Exercise:**Problem:**

A 0.500-g sample of KCl is added to 50.0 g of water in a calorimeter ([\[link\]](#)). If the temperature decreases by 1.05 °C, what is the approximate amount of heat involved in the dissolution of the KCl, assuming the specific heat of the resulting solution is 4.18 J/g °C? Is the reaction exothermic or endothermic?

Exercise:**Problem:**

Dissolving 3.0 g of CaCl₂(s) in 150.0 g of water in a calorimeter ([\[link\]](#)) at 22.4 °C causes the temperature to rise to 25.8 °C. What is the approximate amount of heat involved in the dissolution, assuming the specific heat of the resulting solution is 4.18 J/g °C? Is the reaction exothermic or endothermic?

Solution:

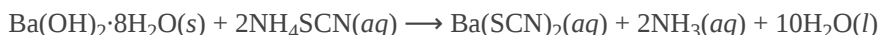
-2.2 kJ; The heat produced shows that the reaction is exothermic.

Exercise:**Problem:**

When 50.0 g of 0.200 M NaCl(aq) at 24.1 °C is added to 100.0 g of 0.100 M AgNO₃(aq) at 24.1 °C in a calorimeter, the temperature increases to 25.2 °C as AgCl(s) forms. Assuming the specific heat of the solution and products is 4.20 J/g °C, calculate the approximate amount of heat in joules produced.

Exercise:**Problem:**

The addition of 3.15 g of Ba(OH)₂·8H₂O to a solution of 1.52 g of NH₄SCN in 100 g of water in a calorimeter caused the temperature to fall by 3.1 °C. Assuming the specific heat of the solution and products is 4.20 J/g °C, calculate the approximate amount of heat absorbed by the reaction, which can be represented by the following equation:

**Solution:**

1.4 kJ

Exercise:

Problem:

The reaction of 50 mL of acid and 50 mL of base described in [\[link\]](#) increased the temperature of the solution by 6.9 degrees C. How much would the temperature have increased if 100 mL of acid and 100 mL of base had been used in the same calorimeter starting at the same temperature of 22.0 °C? Explain your answer.

Exercise:**Problem:**

If the 3.21 g of NH_4NO_3 in [\[link\]](#) were dissolved in 100.0 g of water under the same conditions, how much would the temperature change? Explain your answer.

Solution:

22.6. Since the mass and the heat capacity of the solution is approximately equal to that of the water, the two-fold increase in the amount of water leads to a two-fold decrease of the temperature change.

Exercise:**Problem:**

When 1.0 g of fructose, $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$, a sugar commonly found in fruits, is burned in oxygen in a bomb calorimeter, the temperature of the calorimeter increases by 1.58 °C. If the heat capacity of the calorimeter and its contents is 9.90 kJ/°C, what is q for this combustion?

Exercise:**Problem:**

When a 0.740-g sample of trinitrotoluene (TNT), $\text{C}_7\text{H}_5\text{N}_2\text{O}_6$, is burned in a bomb calorimeter, the temperature increases from 23.4 °C to 26.9 °C. The heat capacity of the calorimeter is 534 J/°C, and it contains 675 mL of water. How much heat was produced by the combustion of the TNT sample?

Solution:

11.7 kJ

Exercise:**Problem:**

One method of generating electricity is by burning coal to heat water, which produces steam that drives an electric generator. To determine the rate at which coal is to be fed into the burner in this type of plant, the heat of combustion per ton of coal must be determined using a bomb calorimeter. When 1.00 g of coal is burned in a bomb calorimeter ([\[link\]](#)), the temperature increases by 1.48 °C. If the heat capacity of the calorimeter is 21.6 kJ/°C, determine the heat produced by combustion of a ton of coal (2.000×10^3 pounds).

Exercise:**Problem:**

The amount of fat recommended for someone with a daily diet of 2000 Calories is 65 g. What percent of the calories in this diet would be supplied by this amount of fat if the average number of Calories for fat is 9.1 Calories/g?

Solution:

30%

Exercise:**Problem:**

A teaspoon of the carbohydrate sucrose (common sugar) contains 16 Calories (16 kcal). What is the mass of one teaspoon of sucrose if the average number of Calories for carbohydrates is 4.1 Calories/g?

Exercise:**Problem:**

What is the maximum mass of carbohydrate in a 6-oz serving of diet soda that contains less than 1 Calorie per can if the average number of Calories for carbohydrates is 4.1 Calories/g?

Solution:

0.24 g

Exercise:**Problem:**

A pint of premium ice cream can contain 1100 Calories. What mass of fat, in grams and pounds, must be produced in the body to store an extra 1.1×10^3 Calories if the average number of Calories for fat is 9.1 Calories/g?

Exercise:**Problem:**

A serving of a breakfast cereal contains 3 g of protein, 18 g of carbohydrates, and 6 g of fat. What is the Calorie content of a serving of this cereal if the average number of Calories for fat is 9.1 Calories/g, for carbohydrates is 4.1 Calories/g, and for protein is 4.1 Calories/g?

Solution:

1.4×10^2 Calories

Exercise:**Problem:**

Which is the least expensive source of energy in kilojoules per dollar: a box of breakfast cereal that weighs 32 ounces and costs \$4.23, or a liter of isooctane (density, 0.6919 g/mL) that costs \$0.45? Compare the nutritional value of the cereal with the heat produced by combustion of the isooctane under standard conditions. A 1.0-ounce serving of the cereal provides 130 Calories.

Glossary

bomb calorimeter

device designed to measure the energy change for processes occurring under conditions of constant volume; commonly used for reactions involving solid and gaseous reactants or products

calorimeter

device used to measure the amount of heat absorbed or released in a chemical or physical process

calorimetry

process of measuring the amount of heat involved in a chemical or physical process

nutritional calorie (Calorie)

unit used for quantifying energy provided by digestion of foods, defined as 1000 cal or 1 kcal

surroundings

all matter other than the system being studied

system

portion of matter undergoing a chemical or physical change being studied

Enthalpy

By the end of this section, you will be able to:

- State the first law of thermodynamics
- Define enthalpy and explain its classification as a state function
- Write and balance thermochemical equations
- Calculate enthalpy changes for various chemical reactions
- Explain Hess's law and use it to compute reaction enthalpies

Thermochemistry is a branch of **chemical thermodynamics**, the science that deals with the relationships between heat, work, and other forms of energy in the context of chemical and physical processes. As we concentrate on thermochemistry in this chapter, we need to consider some widely used concepts of thermodynamics.

Substances act as reservoirs of energy, meaning that energy can be added to them or removed from them. Energy is stored in a substance when the kinetic energy of its atoms or molecules is raised. The greater kinetic energy may be in the form of increased translations (travel or straight-line motions), vibrations, or rotations of the atoms or molecules. When thermal energy is lost, the intensities of these motions decrease and the kinetic energy falls. The total of all possible kinds of energy present in a substance is called the **internal energy (U)**, sometimes symbolized as E .

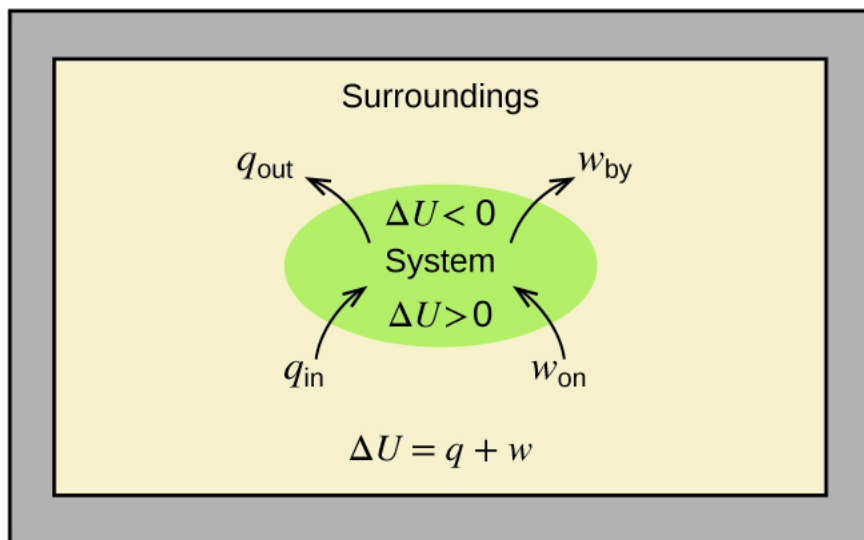
As a system undergoes a change, its internal energy can change, and energy can be transferred from the system to the surroundings, or from the surroundings to the system. Energy is transferred into a system when it absorbs heat (q) from the surroundings or when the surroundings do work (w) on the system. For example, energy is transferred into room-temperature metal wire if it is immersed in hot water (the wire absorbs heat from the water), or if you rapidly bend the wire back and forth (the wire becomes warmer because of the work done on it). Both processes increase the internal energy of the wire, which is reflected in an increase in the wire's temperature. Conversely, energy is transferred out of a system when heat is lost from the system, or when the system does work on the surroundings.

The relationship between internal energy, heat, and work can be represented by the equation:

Equation:

$$\Delta U = q + w$$

as shown in [\[link\]](#). This is one version of the **first law of thermodynamics**, and it shows that the internal energy of a system changes through heat flow into or out of the system (positive q is heat flow in; negative q is heat flow out) or work done on or by the system. The work, w , is positive if it is done on the system and negative if it is done by the system.



The internal energy, U , of a system can be changed by heat flow and work.

If heat flows into the system, q_{in} , or work is done on the system, w_{on} , its internal energy increases, $\Delta U > 0$. If heat flows out of the system, q_{out} , or work is done by the system, w_{by} , its internal energy decreases, $\Delta U < 0$.

A type of work called **expansion work** (or pressure-volume work) occurs when a system pushes back the surroundings against a restraining pressure, or when the surroundings compress the system. An example of this occurs during the operation of an internal combustion engine. The reaction of gasoline and oxygen is exothermic. Some of this energy is given off as heat, and some does work pushing the piston in the cylinder. The substances involved in the reaction are the system, and the engine and the rest of the universe are the surroundings. The system loses energy by both heating and doing work on the surroundings, and its internal energy decreases. (The engine is able to keep the car moving because this process is repeated many times per second while the engine is running.) We will consider how to determine the amount of work involved in a chemical or physical change in the chapter on thermodynamics.

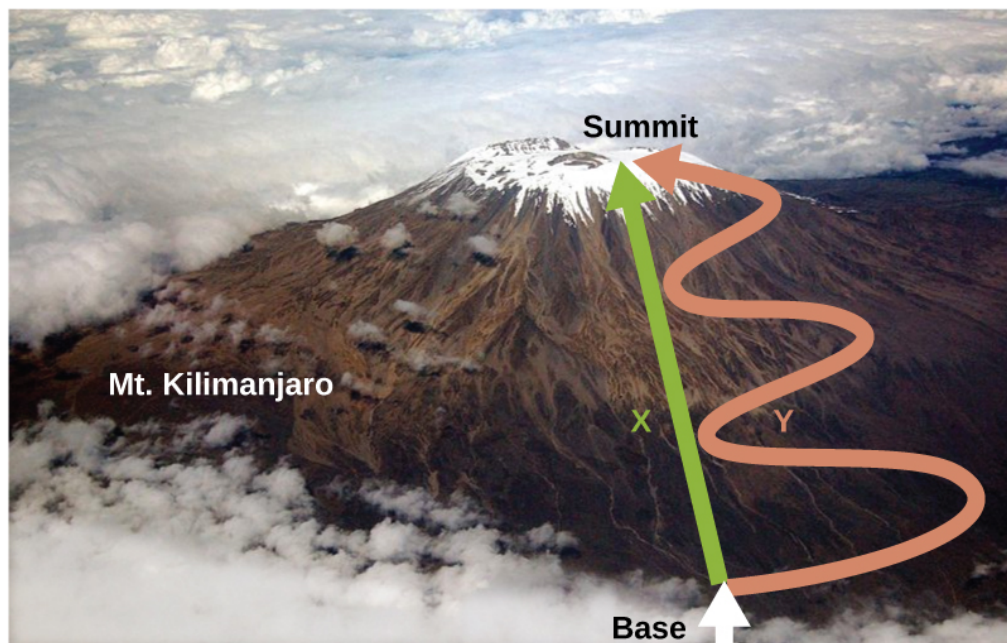
Note:



This view of [an internal combustion engine](#) illustrates the conversion of energy produced by the exothermic combustion reaction of a fuel such as gasoline into energy of motion.

As discussed, the relationship between internal energy, heat, and work can be represented as $\Delta U = q + w$. Internal energy is a type of quantity known as a **state function** (or state variable), whereas heat and work are not state functions. The value of a state function depends only on the state that a system is in, and not on how that state is

reached. If a quantity is not a state function, then its value *does* depend on how the state is reached. An example of a state function is altitude or elevation. If you stand on the summit of Mt. Kilimanjaro, you are at an altitude of 5895 m, and it does not matter whether you hiked there or parachuted there. The distance you traveled to the top of Kilimanjaro, however, is not a state function. You could climb to the summit by a direct route or by a more roundabout, circuitous path ([link](#)). The distances traveled would differ (distance is not a state function) but the elevation reached would be the same (altitude is a state function).



Paths X and Y represent two different routes to the summit of Mt. Kilimanjaro. Both have the same change in elevation (altitude or elevation on a mountain is a state function; it does not depend on path), but they have very different distances traveled (distance walked is not a state function; it depends on the path). (credit: modification of work by Paul Shaffner)

Chemists ordinarily use a property known as **enthalpy (H)** to describe the thermodynamics of chemical and physical processes. Enthalpy is defined as the sum of a system's internal energy (U) and the mathematical product of its pressure (P) and volume (V):

Equation:

$$H = U + PV$$

Since it is derived from three state functions (U , P , and V), enthalpy is also a state function. Enthalpy values for specific substances cannot be measured directly; only enthalpy *changes* for chemical or physical processes can be determined. For processes that take place at constant pressure (a common condition for many chemical and physical changes), the **enthalpy change (ΔH)** is:

Equation:

$$\Delta H = \Delta U + P\Delta V$$

The mathematical product $P\Delta V$ represents work (w), namely, expansion or pressure-volume work as noted. By their definitions, the arithmetic signs of ΔV and w will always be opposite:

Equation:

$$P\Delta V = -w$$

Substituting this equation and the definition of internal energy into the enthalpy-change equation yields:

Equation:

$$\begin{aligned}\Delta H &= \Delta U + P\Delta V \\ &= q_p + w - w \\ &= q_p\end{aligned}$$

where q_p is the heat of reaction under conditions of constant pressure.

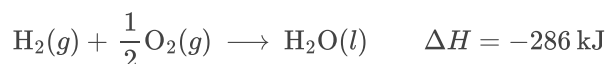
And so, if a chemical or physical process is carried out at constant pressure with the only work done caused by expansion or contraction, then the heat flow (q_p) and enthalpy change (ΔH) for the process are equal.

The heat given off when you operate a Bunsen burner is equal to the enthalpy change of the methane combustion reaction that takes place, since it occurs at the essentially constant pressure of the atmosphere. On the other hand, the heat produced by a reaction measured in a bomb calorimeter ([link](#)) is not equal to ΔH because the closed, constant-volume metal container prevents expansion work from occurring. Chemists usually perform experiments under normal atmospheric conditions, at constant external pressure with $q = \Delta H$, which makes enthalpy the most convenient choice for determining heat.

The following conventions apply when we use ΔH :

1. Chemists use a thermochemical equation to represent the changes in both matter and energy. In a thermochemical equation, the enthalpy change of a reaction is shown as a ΔH value following the equation for the reaction. This ΔH value indicates the amount of heat associated with the reaction involving the number of moles of reactants and products *as shown in the chemical equation*. For example, consider this equation:

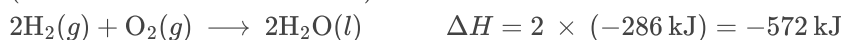
Equation:



This equation indicates that when 1 mole of hydrogen gas and $\frac{1}{2}$ mole of oxygen gas at some temperature and pressure change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released to the surroundings. If the coefficients of the chemical equation are multiplied by some factor, the enthalpy change must be multiplied by that same factor (ΔH is an extensive property):

Equation:

(two-fold increase in amounts)

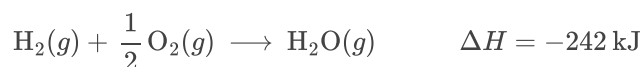


(two-fold decrease in amounts)



2. The enthalpy change of a reaction depends on the physical state of the reactants and products of the reaction (whether we have gases, liquids, solids, or aqueous solutions), so these must be shown. For example, when 1 mole of hydrogen gas and $\frac{1}{2}$ mole of oxygen gas change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released. If gaseous water forms, only 242 kJ of heat are released.

Equation:



3. A negative value of an enthalpy change, ΔH , indicates an exothermic reaction; a positive value of ΔH indicates an endothermic reaction. If the direction of a chemical equation is reversed, the arithmetic sign of its ΔH is changed (a process that is endothermic in one direction is exothermic in the opposite direction).

Example:

Measurement of an Enthalpy Change

When 0.0500 mol of $\text{HCl}(aq)$ reacts with 0.0500 mol of $\text{NaOH}(aq)$ to form 0.0500 mol of $\text{NaCl}(aq)$, 2.9 kJ of heat are produced. What is the enthalpy, ΔH , per mole of acid that reacts?

Equation:



Solution

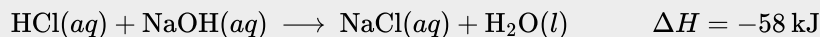
For the reaction of 0.0500 mol acid (HCl), $q = -2.9$ kJ. This ratio $\frac{-2.9 \text{ kJ}}{0.0500 \text{ mol HCl}}$ can be used as a conversion factor to find the heat produced when 1 mole of HCl reacts:

Equation:

$$\Delta H = 1 \text{ mol HCl} \times \frac{-2.9 \text{ kJ}}{0.0500 \text{ mol HCl}} = -58 \text{ kJ}$$

The enthalpy change when 1 mole of HCl reacts is -58 kJ. Since that is the number of moles in the chemical equation, we write the thermochemical equation as:

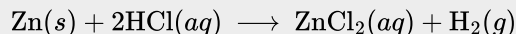
Equation:



Check Your Learning

When 1.34 g $\text{Zn}(s)$ reacts with 60.0 mL of 0.750 M $\text{HCl}(aq)$, 3.14 kJ of heat are produced. Determine the enthalpy change per mole of zinc reacting for the reaction:

Equation:



Note:

Answer:

$$\Delta H = -153 \text{ kJ}$$

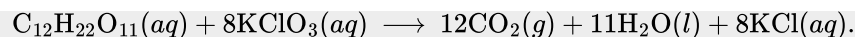
Be sure to take both stoichiometry and limiting reactants into account when determining the ΔH for a chemical reaction.

Example:

Another Example of the Measurement of an Enthalpy Change

A gummy bear contains 2.67 g sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$. When it reacts with 7.19 g potassium chlorate, KClO_3 , 43.7 kJ of heat are produced. Determine the enthalpy change for the reaction

Equation:



Solution

We have $2.67 \text{ g} \times \frac{1 \text{ mol}}{342.3 \text{ g}} = 0.00780 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}$ available, and

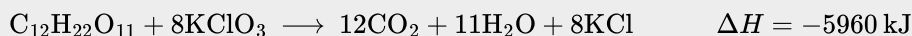
$7.19 \text{ g} \times \frac{1 \text{ mol}}{122.5 \text{ g}} = 0.0587 \text{ mol KClO}_3$ available. Since

$0.0587 \text{ mol KClO}_3 \times \frac{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{8 \text{ mol KClO}_3} = 0.00734 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}$ is needed, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ is the excess reactant and KClO_3 is the limiting reactant.

The reaction uses 8 mol KClO_3 , and the conversion factor is $\frac{-43.7 \text{ kJ}}{0.0587 \text{ mol KClO}_3}$, so we have

$\Delta H = 8 \text{ mol} \times \frac{-43.7 \text{ kJ}}{0.0587 \text{ mol KClO}_3} = -5960 \text{ kJ}$. The enthalpy change for this reaction is -5960 kJ , and the thermochemical equation is:

Equation:



Check Your Learning

When 1.42 g of iron reacts with 1.80 g of chlorine, 3.22 g of $\text{FeCl}_2(s)$ and 8.60 kJ of heat is produced. What is the enthalpy change for the reaction when 1 mole of $\text{FeCl}_2(s)$ is produced?

Note:

Answer:

$\Delta H = -338 \text{ kJ}$

Enthalpy changes are typically tabulated for reactions in which both the reactants and products are at the same conditions. A **standard state** is a commonly accepted set of conditions used as a reference point for the determination of properties under other different conditions. For chemists, the IUPAC standard state refers to materials under a pressure of 1 bar and solutions at 1 M, and does not specify a temperature. Many thermochemical tables list values with a standard state of 1 atm. Because the ΔH of a reaction changes very little with such small changes in pressure (1 bar = 0.987 atm), ΔH values (except for the most precisely measured values) are essentially the same under both sets of standard conditions. We will include a superscripted “o” in the enthalpy change symbol to designate standard state. Since the usual (but not technically standard) temperature is 298.15 K, we will use a subscripted “298” to designate this temperature. Thus, the symbol (ΔH_{298}°) is used to indicate an enthalpy change for a process occurring under these conditions. (The symbol ΔH is used to indicate an enthalpy change for a reaction occurring under nonstandard conditions.)

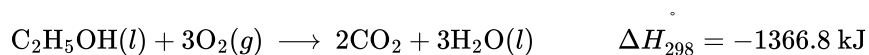
The enthalpy changes for many types of chemical and physical processes are available in the reference literature, including those for combustion reactions, phase transitions, and formation reactions. As we discuss these quantities, it is important to pay attention to the *extensive* nature of enthalpy and enthalpy changes. Since the enthalpy change for a given reaction is proportional to the amounts of substances involved, it may be reported on that basis (i.e., as the ΔH for specific amounts of reactants). However, we often find it more useful to divide one extensive property (ΔH) by another (amount of substance), and report a per-amount *intensive* value of ΔH , often “normalized” to a per-mole basis. (Note that this is similar to determining the intensive property specific heat from the extensive property heat capacity, as seen previously.)

Enthalpy of Combustion

Standard enthalpy of combustion (ΔH_C°) is the enthalpy change when 1 mole of a substance burns (combines vigorously with oxygen) under standard state conditions; it is sometimes called “heat of combustion.” For

example, the enthalpy of combustion of ethanol, -1366.8 kJ/mol , is the amount of heat produced when one mole of ethanol undergoes complete combustion at 25°C and 1 atmosphere pressure, yielding products also at 25°C and 1 atm.

Equation:



Enthalpies of combustion for many substances have been measured; a few of these are listed in [\[link\]](#). Many readily available substances with large enthalpies of combustion are used as fuels, including hydrogen, carbon (as coal or charcoal), and **hydrocarbons** (compounds containing only hydrogen and carbon), such as methane, propane, and the major components of gasoline.

Standard Molar Enthalpies of Combustion		
Substance	Combustion Reaction	Enthalpy of Combustion, $\Delta H_c^\circ (\frac{\text{kJ}}{\text{mol}}$ at 25°C)
carbon	$\text{C}(s) + \text{O}_2(g) \longrightarrow \text{CO}_2(g)$	-393.5
hydrogen	$\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \longrightarrow \text{H}_2\text{O}(l)$	-285.8
magnesium	$\text{Mg}(s) + \frac{1}{2} \text{O}_2(g) \longrightarrow \text{MgO}(s)$	-601.6
sulfur	$\text{S}(s) + \text{O}_2(g) \longrightarrow \text{SO}_2(g)$	-296.8
carbon monoxide	$\text{CO}(g) + \frac{1}{2} \text{O}_2(g) \longrightarrow \text{CO}_2(g)$	-283.0
methane	$\text{CH}_4(g) + 2\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$	-890.8
acetylene	$\text{C}_2\text{H}_2(g) + \frac{5}{2} \text{O}_2(g) \longrightarrow 2\text{CO}_2(g) + \text{H}_2\text{O}(l)$	-1301.1
ethanol	$\text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) \longrightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l)$	-1366.8
methanol	$\text{CH}_3\text{OH}(l) + \frac{3}{2} \text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$	-726.1
isooctane	$\text{C}_8\text{H}_{18}(l) + \frac{25}{2} \text{O}_2(g) \longrightarrow 8\text{CO}_2(g) + 9\text{H}_2\text{O}(l)$	-5461

Example:

Using Enthalpy of Combustion

As [\[link\]](#) suggests, the combustion of gasoline is a highly exothermic process. Let us determine the approximate amount of heat produced by burning 1.00 L of gasoline, assuming the enthalpy of combustion of gasoline is the same as that of isooctane, a common component of gasoline. The density of isooctane is 0.692 g/mL .



The combustion of gasoline is very exothermic. (credit: modification of work by “AlexEagle”/Flickr)

Solution

Starting with a known amount (1.00 L of isooctane), we can perform conversions between units until we arrive at the desired amount of heat or energy. The enthalpy of combustion of isooctane provides one of the necessary conversions. [link](#) gives this value as -5460 kJ per 1 mole of isooctane (C_8H_{18}).

Using these data,

Equation:

$$1.00 \text{ L C}_8\text{H}_{18} \times \frac{1000 \text{ mL C}_8\text{H}_{18}}{1 \text{ L C}_8\text{H}_{18}} \times \frac{0.692 \text{ g C}_8\text{H}_{18}}{1 \text{ mL C}_8\text{H}_{18}} \times \frac{1 \text{ mol C}_8\text{H}_{18}}{114 \text{ g C}_8\text{H}_{18}} \times \frac{-5460 \text{ kJ}}{1 \text{ mol C}_8\text{H}_{18}} = -3.31 \times 10^4 \text{ kJ}$$

The combustion of 1.00 L of isooctane produces 33,100 kJ of heat. (This amount of energy is enough to melt 99.2 kg, or about 218 lbs, of ice.)

Note: If you do this calculation one step at a time, you would find:

Equation:

$$1.00 \text{ L C}_8\text{H}_{18} \longrightarrow 1.00 \times 10^3 \text{ mL C}_8\text{H}_{18}$$

$$1.00 \times 10^3 \text{ mL C}_8\text{H}_{18} \longrightarrow 692 \text{ g C}_8\text{H}_{18}$$

$$692 \text{ g C}_8\text{H}_{18} \longrightarrow 6.07 \text{ mol C}_8\text{H}_{18}$$

$$692 \text{ g C}_8\text{H}_{18} \longrightarrow -3.31 \times 10^4 \text{ kJ}$$

Check Your Learning

How much heat is produced by the combustion of 125 g of acetylene?

Note:

Answer:

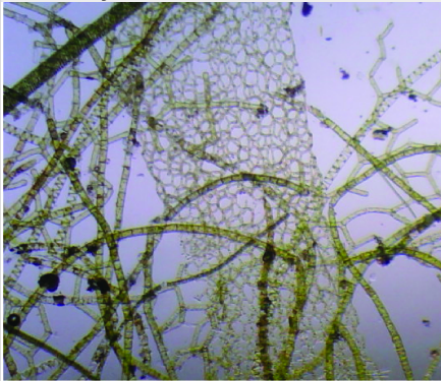
$$6.25 \times 10^3 \text{ kJ}$$

Note:

Emerging Algae-Based Energy Technologies (Biofuels)

As reserves of fossil fuels diminish and become more costly to extract, the search is ongoing for replacement fuel sources for the future. Among the most promising biofuels are those derived from algae ([link](#)). The species of algae used are nontoxic, biodegradable, and among the world's fastest growing organisms. About 50% of algal weight is oil, which can be readily converted into fuel such as biodiesel. Algae can yield 26,000 gallons of biofuel

per hectare—much more energy per acre than other crops. Some strains of algae can flourish in brackish water that is not usable for growing other crops. Algae can produce biodiesel, biogasoline, ethanol, butanol, methane, and even jet fuel.



(a)



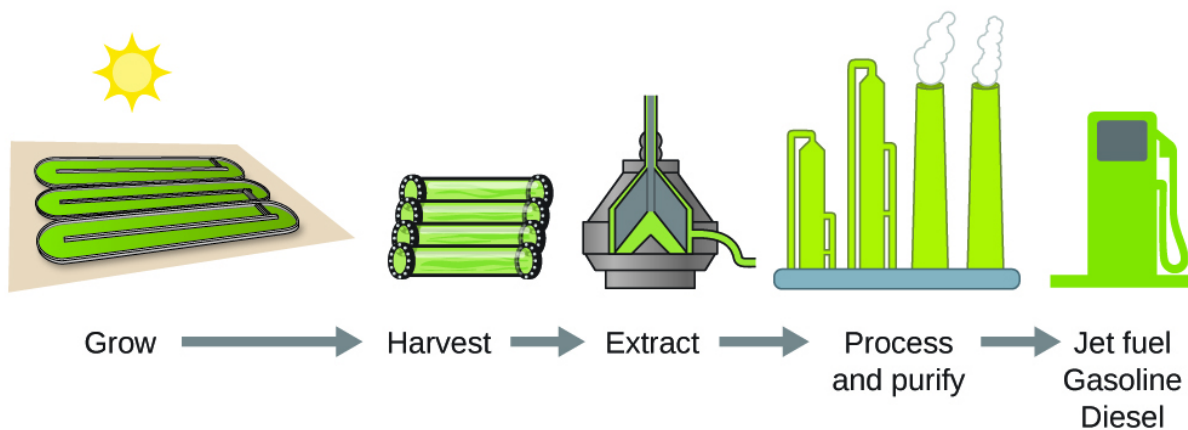
(b)



(c)

(a) Tiny algal organisms can be (b) grown in large quantities and eventually (c) turned into a useful fuel such as biodiesel. (credit a: modification of work by Micah Sittig; credit b: modification of work by Robert Kerton; credit c: modification of work by John F. Williams)

According to the US Department of Energy, only 39,000 square kilometers (about 0.4% of the land mass of the US or less than $\frac{1}{7}$ of the area used to grow corn) can produce enough algal fuel to replace all the petroleum-based fuel used in the US. The cost of algal fuels is becoming more competitive—for instance, the US Air Force is producing jet fuel from algae at a total cost of under \$5 per gallon.^[footnote] The process used to produce algal fuel is as follows: grow the algae (which use sunlight as their energy source and CO₂ as a raw material); harvest the algae; extract the fuel compounds (or precursor compounds); process as necessary (e.g., perform a transesterification reaction to make biodiesel); purify; and distribute ([link](http://www.theguardian.com/environment/2010/feb/13/algae-solve-pentagon-fuel-problem)). For more on algal fuel, see <http://www.theguardian.com/environment/2010/feb/13/algae-solve-pentagon-fuel-problem>.



Algae convert sunlight and carbon dioxide into oil that is harvested, extracted, purified, and transformed into a variety of renewable fuels.

Note:



Click [here](#) to learn more about the process of creating algae biofuel.

Standard Enthalpy of Formation

A **standard enthalpy of formation** ΔH_f° is an enthalpy change for a reaction in which exactly 1 mole of a pure substance is formed from free elements in their most stable states under standard state conditions. These values are especially useful for computing or predicting enthalpy changes for chemical reactions that are impractical or dangerous to carry out, or for processes for which it is difficult to make measurements. If we have values for the appropriate standard enthalpies of formation, we can determine the enthalpy change for any reaction, which we will practice in the next section on Hess's law.

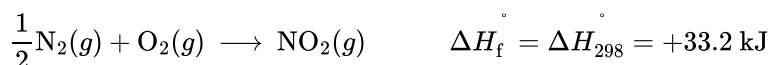
The standard enthalpy of formation of $\text{CO}_2(g)$ is -393.5 kJ/mol . This is the enthalpy change for the exothermic reaction:

Equation:



starting with the reactants at a pressure of 1 atm and 25°C (with the carbon present as graphite, the most stable form of carbon under these conditions) and ending with one mole of CO_2 , also at 1 atm and 25°C . For nitrogen dioxide, $\text{NO}_2(g)$, ΔH_f° is 33.2 kJ/mol . This is the enthalpy change for the reaction:

Equation:



A reaction equation with $\frac{1}{2}$ mole of N_2 and 1 mole of O_2 is correct in this case because the standard enthalpy of formation always refers to 1 mole of product, $\text{NO}_2(g)$.

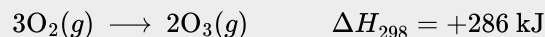
You will find a table of standard enthalpies of formation of many common substances in [Appendix G](#). These values indicate that formation reactions range from highly exothermic (such as -2984 kJ/mol for the formation of P_4O_{10}) to strongly endothermic (such as $+226.7 \text{ kJ/mol}$ for the formation of acetylene, C_2H_2). By definition, the standard enthalpy of formation of an element in its most stable form is equal to zero under standard conditions, which is 1 atm for gases and 1 M for solutions.

Example:

Evaluating an Enthalpy of Formation

Ozone, $\text{O}_3(g)$, forms from oxygen, $\text{O}_2(g)$, by an endothermic process. Ultraviolet radiation is the source of the energy that drives this reaction in the upper atmosphere. Assuming that both the reactants and products of the reaction are in their standard states, determine the standard enthalpy of formation, ΔH_f° of ozone from the following information:

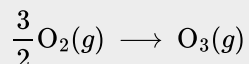
Equation:



Solution

ΔH_f° is the enthalpy change for the formation of one mole of a substance in its standard state from the elements in their standard states. Thus, ΔH_f° for $\text{O}_3(g)$ is the enthalpy change for the reaction:

Equation:



For the formation of 2 mol of $\text{O}_3(g)$, $\Delta H_{298}^\circ = +286 \text{ kJ}$. This ratio, $\left(\frac{286 \text{ kJ}}{2 \text{ mol O}_3}\right)$, can be used as a conversion factor to find the heat produced when 1 mole of $\text{O}_3(g)$ is formed, which is the enthalpy of formation for $\text{O}_3(g)$:

Equation:

$$\Delta H^\circ \text{ for 1 mole of O}_3(g) = 1 \text{ mol O}_3 \times \frac{286 \text{ kJ}}{2 \text{ mol O}_3} = 143 \text{ kJ}$$

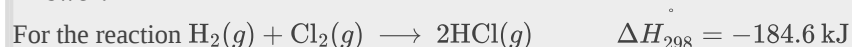
Therefore, $\Delta H_f^\circ [\text{O}_3(g)] = +143 \text{ kJ/mol}$.

Check Your Learning

Hydrogen gas, H_2 , reacts explosively with gaseous chlorine, Cl_2 , to form hydrogen chloride, $\text{HCl}(g)$. What is the enthalpy change for the reaction of 1 mole of $\text{H}_2(g)$ with 1 mole of $\text{Cl}_2(g)$ if both the reactants and products are at standard state conditions? The standard enthalpy of formation of $\text{HCl}(g)$ is -92.3 kJ/mol .

Note:

Answer:



Example:

Writing Reaction Equations for ΔH_f°

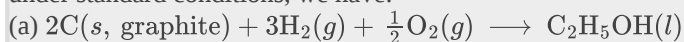
Write the heat of formation reaction equations for:

(a) $\text{C}_2\text{H}_5\text{OH}(l)$

(b) $\text{Ca}_3(\text{PO}_4)_2(s)$

Solution

Remembering that ΔH_f° reaction equations are for forming 1 mole of the compound from its constituent elements under standard conditions, we have:



Note: The standard state of carbon is graphite, and phosphorus exists as P_4 .

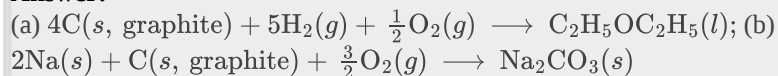
Check Your Learning

Write the heat of formation reaction equations for:

(a) $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5(l)$

(b) $\text{Na}_2\text{CO}_3(s)$

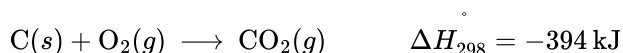
Note:

Answer:**Hess's Law**

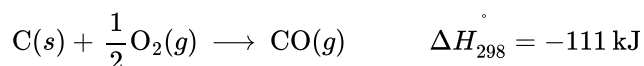
There are two ways to determine the amount of heat involved in a chemical change: measure it experimentally, or calculate it from other experimentally determined enthalpy changes. Some reactions are difficult, if not impossible, to investigate and make accurate measurements for experimentally. And even when a reaction is not hard to perform or measure, it is convenient to be able to determine the heat involved in a reaction without having to perform an experiment.

This type of calculation usually involves the use of **Hess's law**, which states: *If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps.* Hess's law is valid because enthalpy is a state function: Enthalpy changes depend only on where a chemical process starts and ends, but not on the path it takes from start to finish. For example, we can think of the reaction of carbon with oxygen to form carbon dioxide as occurring either directly or by a two-step process.

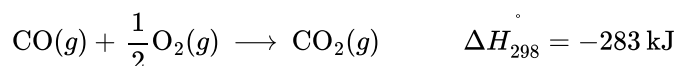
The direct process is written:

Equation:

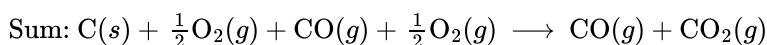
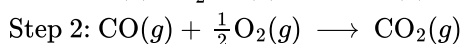
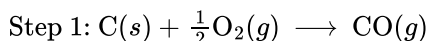
In the two-step process, first carbon monoxide is formed:

Equation:

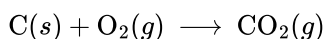
Then, carbon monoxide reacts further to form carbon dioxide:

Equation:

The equation describing the overall reaction is the sum of these two chemical changes:

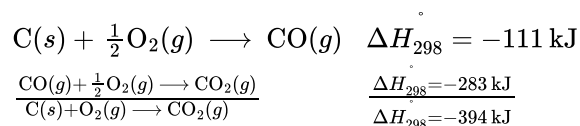
Equation:

Because the CO produced in Step 1 is consumed in Step 2, the net change is:

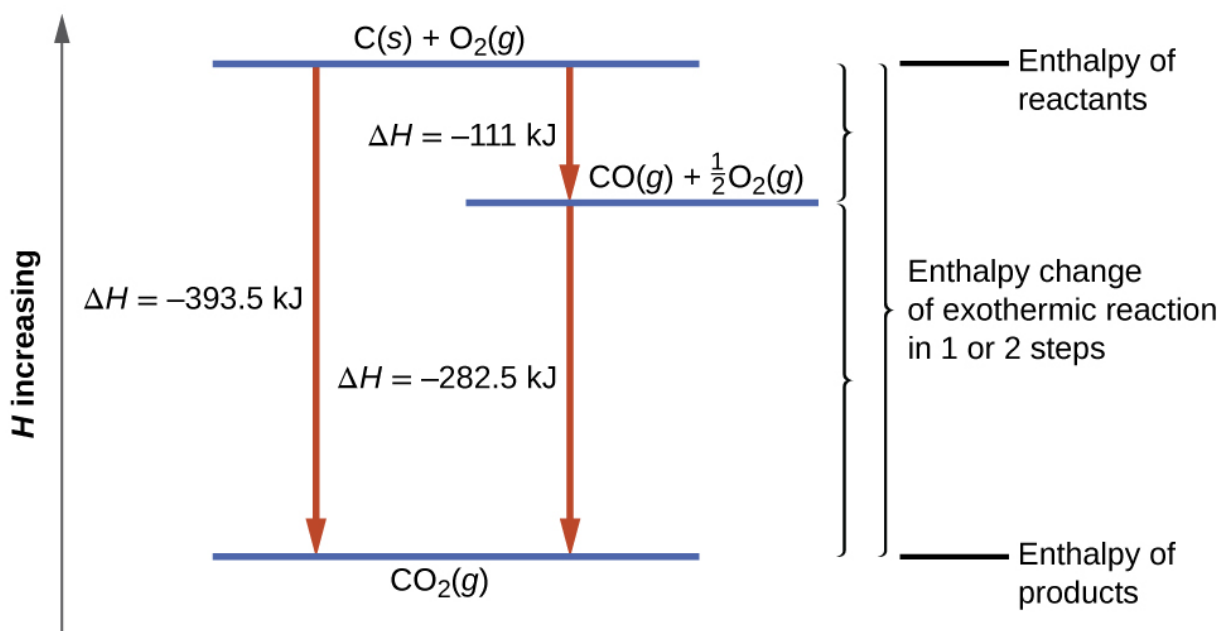
Equation:

According to Hess's law, the enthalpy change of the reaction will equal the sum of the enthalpy changes of the steps. We can apply the data from the experimental enthalpies of combustion in [\[link\]](#) to find the enthalpy change of the entire reaction from its two steps:

Equation:



The result is shown in [\[link\]](#). We see that ΔH of the overall reaction is the same whether it occurs in one step or two. This finding (overall ΔH for the reaction = sum of ΔH values for reaction "steps" in the overall reaction) is true in general for chemical and physical processes.

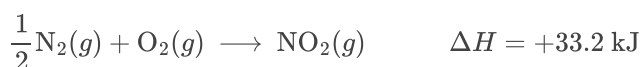


The formation of $\text{CO}_2(g)$ from its elements can be thought of as occurring in two steps, which sum to the overall reaction, as described by Hess's law. The horizontal blue lines represent enthalpies. For an exothermic process, the products are at lower enthalpy than are the reactants.

Before we further practice using Hess's law, let us recall two important features of ΔH .

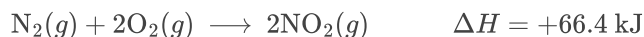
1. ΔH is directly proportional to the quantities of reactants or products. For example, the enthalpy change for the reaction forming 1 mole of $\text{NO}_2(g)$ is +33.2 kJ:

Equation:



When 2 moles of NO_2 (twice as much) are formed, the ΔH will be twice as large:

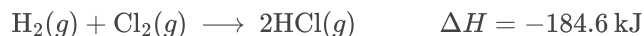
Equation:



In general, if we multiply or divide an equation by a number, then the enthalpy change should also be multiplied or divided by the same number.

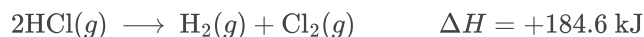
2. ΔH for a reaction in one direction is equal in magnitude and opposite in sign to ΔH for the reaction in the reverse direction. For example, given that:

Equation:



Then, for the “reverse” reaction, the enthalpy change is also “reversed”:

Equation:

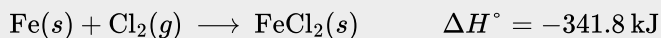


Example:

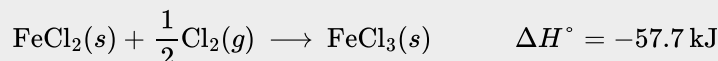
Stepwise Calculation of ΔH_f° Using Hess’s Law

Determine the enthalpy of formation, ΔH_f° , of $\text{FeCl}_3(s)$ from the enthalpy changes of the following two-step process that occurs under standard state conditions:

Equation:



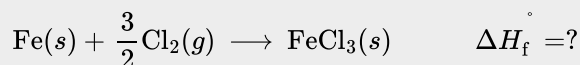
Equation:



Solution

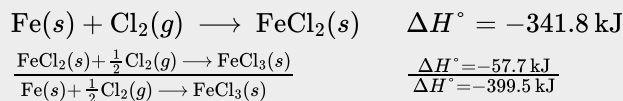
We are trying to find the standard enthalpy of formation of $\text{FeCl}_3(s)$, which is equal to ΔH° for the reaction:

Equation:



Looking at the reactions, we see that the reaction for which we want to find ΔH° is the sum of the two reactions with known ΔH values, so we must sum their ΔH s:

Equation:

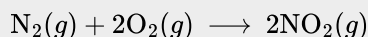


The enthalpy of formation, ΔH_f° , of $\text{FeCl}_3(s)$ is -399.5 kJ/mol .

Check Your Learning

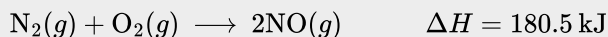
Calculate ΔH for the process:

Equation:

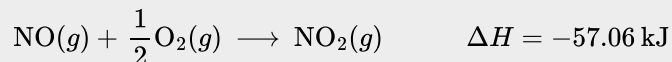


from the following information:

Equation:



Equation:



Note:

Answer:

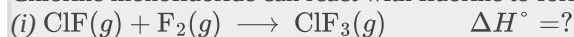
66.4 kJ

Here is a less straightforward example that illustrates the thought process involved in solving many Hess's law problems. It shows how we can find many standard enthalpies of formation (and other values of ΔH) if they are difficult to determine experimentally.

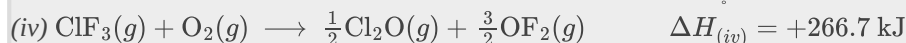
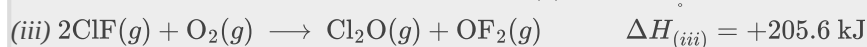
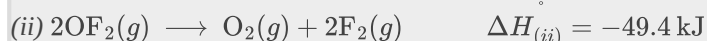
Example:

A More Challenging Problem Using Hess's Law

Chlorine monofluoride can react with fluorine to form chlorine trifluoride:



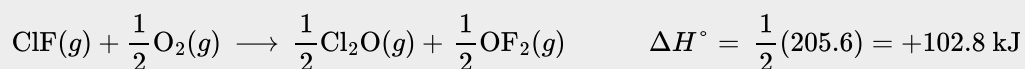
Use the reactions here to determine the ΔH° for reaction (i):



Solution

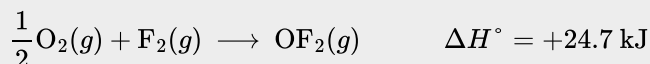
Our goal is to manipulate and combine reactions (ii), (iii), and (iv) such that they add up to reaction (i). Going from left to right in (i), we first see that $\text{ClF}(g)$ is needed as a reactant. This can be obtained by multiplying reaction (iii) by $\frac{1}{2}$, which means that the ΔH° change is also multiplied by $\frac{1}{2}$:

Equation:



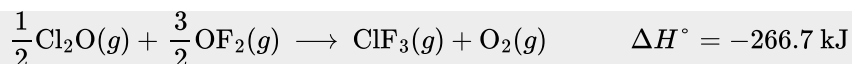
Next, we see that F_2 is also needed as a reactant. To get this, reverse and halve reaction (ii), which means that the ΔH° changes sign and is halved:

Equation:



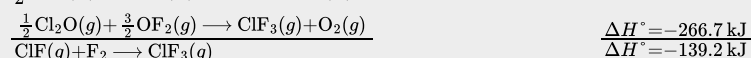
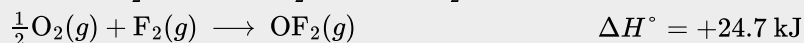
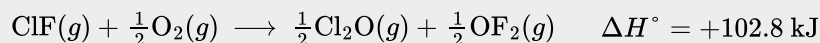
To get ClF_3 as a product, reverse (iv), changing the sign of ΔH° :

Equation:



Now check to make sure that these reactions add up to the reaction we want:

Equation:



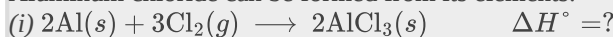
Reactants $\frac{1}{2}\text{O}_2$ and $\frac{1}{2}\text{O}_2$ cancel out product O_2 ; product $\frac{1}{2}\text{Cl}_2\text{O}$ cancels reactant $\frac{1}{2}\text{Cl}_2\text{O}$; and reactant $\frac{3}{2}\text{OF}_2$ is cancelled by products $\frac{1}{2}\text{OF}_2$ and OF_2 . This leaves only reactants $\text{ClF}(g)$ and $\text{F}_2(g)$ and product $\text{ClF}_3(g)$, which are what we want. Since summing these three modified reactions yields the reaction of interest, summing the three modified ΔH° values will give the desired ΔH° :

Equation:

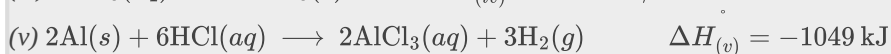
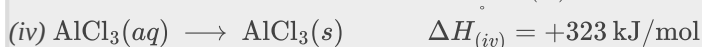
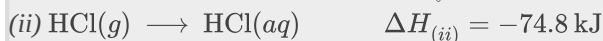
$$\Delta H^\circ = (+102.8 \text{ kJ}) + (24.7 \text{ kJ}) + (-266.7 \text{ kJ}) = -139.2 \text{ kJ}$$

Check Your Learning

Aluminum chloride can be formed from its elements:



Use the reactions here to determine the ΔH° for reaction (i):



Note:

Answer:

-1407 kJ

We also can use Hess's law to determine the enthalpy change of any reaction if the corresponding enthalpies of formation of the reactants and products are available. The stepwise reactions we consider are: (i) decompositions of the reactants into their component elements (for which the enthalpy changes are proportional to the negative of the enthalpies of formation of the reactants), followed by (ii) re-combinations of the elements to give the products (with the enthalpy changes proportional to the enthalpies of formation of the products). The standard enthalpy change of the overall reaction is therefore equal to: (ii) the sum of the standard enthalpies of formation of all the products plus (i) the sum of the negatives of the standard enthalpies of formation of the reactants. This is usually rearranged slightly to be written as follows, with Σ representing "the sum of" and n standing for the stoichiometric coefficients:

Equation:

$$\Delta H_{\text{reaction}}^\circ = \sum n \times \Delta H_{\text{f}}^\circ (\text{products}) - \sum n \times \Delta H_{\text{f}}^\circ (\text{reactants})$$

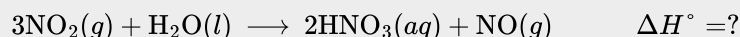
The following example shows in detail why this equation is valid, and how to use it to calculate the enthalpy change for a reaction of interest.

Example:

Using Hess's Law

What is the standard enthalpy change for the reaction:

Equation:



Solution: Using the Equation

Use the special form of Hess's law given previously, and values from [Appendix G](#):

Equation:

$$\Delta H_{\text{reaction}}^\circ = \sum n \times \Delta H_f^\circ(\text{products}) - \sum n \times \Delta H_f^\circ(\text{reactants})$$

Equation:

$$\begin{aligned} &= \left[2 \cancel{\text{mol HNO}_3(aq)} \times \frac{-207.4 \text{ kJ}}{\cancel{\text{mol HNO}_3(aq)}} + 1 \cancel{\text{mol NO}(g)} \times \frac{+90.2 \text{ kJ}}{\cancel{\text{mol NO}(g)}} \right] \\ &- \left[3 \cancel{\text{mol NO}_2(g)} \times \frac{+33.2 \text{ kJ}}{\cancel{\text{mol NO}_2(g)}} + 1 \cancel{\text{mol H}_2\text{O}(l)} \times \frac{-285.8 \text{ kJ}}{\cancel{\text{mol H}_2\text{O}(l)}} \right] \\ &= 2(-207.4 \text{ kJ}) + 1(+90.2 \text{ kJ}) - 3(+33.2 \text{ kJ}) - 1(-285.8 \text{ kJ}) \\ &= -138.4 \text{ kJ} \end{aligned}$$

Solution: Supporting Why the General Equation Is Valid

Alternatively, we can write this reaction as the sum of the decompositions of $3\text{NO}_2(g)$ and $1\text{H}_2\text{O}(l)$ into their constituent elements, and the formation of $2\text{HNO}_3(aq)$ and $1\text{NO}(g)$ from their constituent elements. Writing out these reactions, and noting their relationships to the ΔH_f° values for these compounds (from [Appendix G](#)), we have:

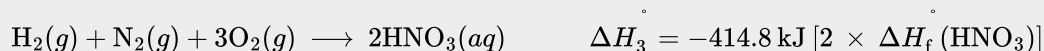
Equation:



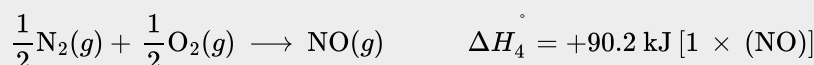
Equation:



Equation:

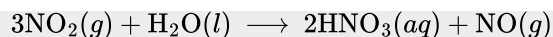


Equation:



Summing these reaction equations gives the reaction we are interested in:

Equation:



Summing their enthalpy changes gives the value we want to determine:

Equation:

$$\begin{aligned}\Delta H_{\text{rxn}}^{\circ} &= \Delta H_1^{\circ} + \Delta H_2^{\circ} + \Delta H_3^{\circ} + \Delta H_4^{\circ} = (-99.6 \text{ kJ}) + (+285.8 \text{ kJ}) + (-414.8 \text{ kJ}) + (+90.2 \text{ kJ}) \\ &= -138.4 \text{ kJ}\end{aligned}$$

So the standard enthalpy change for this reaction is $\Delta H^{\circ} = -138.4 \text{ kJ}$.

Note that this result was obtained by (1) multiplying the ΔH_f° of each product by its stoichiometric coefficient and summing those values, (2) multiplying the ΔH_f° of each reactant by its stoichiometric coefficient and summing those values, and then (3) subtracting the result found in (2) from the result found in (1). This is also the procedure in using the general equation, as shown.

Check Your Learning

Calculate the heat of combustion of 1 mole of ethanol, $\text{C}_2\text{H}_5\text{OH}(l)$, when $\text{H}_2\text{O}(l)$ and $\text{CO}_2(g)$ are formed. Use the following enthalpies of formation: $\text{C}_2\text{H}_5\text{OH}(l)$, -278 kJ/mol ; $\text{H}_2\text{O}(l)$, -286 kJ/mol ; and $\text{CO}_2(g)$, -394 kJ/mol .

Note:

Answer:

-1368 kJ/mol

Key Concepts and Summary

If a chemical change is carried out at constant pressure and the only work done is caused by expansion or contraction, q for the change is called the enthalpy change with the symbol ΔH , or ΔH_{298} for reactions occurring under standard state conditions. The value of ΔH for a reaction in one direction is equal in magnitude, but opposite in sign, to ΔH for the reaction in the opposite direction, and ΔH is directly proportional to the quantity of reactants and products. Examples of enthalpy changes include enthalpy of combustion, enthalpy of fusion, enthalpy of vaporization, and standard enthalpy of formation. The standard enthalpy of formation, ΔH_f° , is the enthalpy change accompanying the formation of 1 mole of a substance from the elements in their most stable states at 1 bar (standard state). Many of the processes are carried out at 298.15 K. If the enthalpies of formation are available for the reactants and products of a reaction, the enthalpy change can be calculated using Hess's law: If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps.

Key Equations

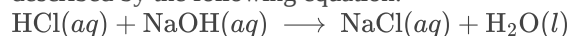
- $\Delta U = q + w$
- $\Delta H_{\text{reaction}}^{\circ} = \sum n \times \Delta H_f^{\circ}(\text{products}) - \sum n \times \Delta H_f^{\circ}(\text{reactants})$

Chemistry End of Chapter Exercises

Exercise:

Problem:

Explain how the heat measured in [\[link\]](#) differs from the enthalpy change for the exothermic reaction described by the following equation:

**Solution:**

The enthalpy change of the indicated reaction is for exactly 1 mol HCL and 1 mol NaOH; the heat in the example is produced by 0.0500 mol HCl and 0.0500 mol NaOH.

Exercise:**Problem:**

Using the data in the check your learning section of [\[link\]](#), calculate ΔH in kJ/mol of $\text{AgNO}_3(aq)$ for the reaction: $\text{NaCl}(aq) + \text{AgNO}_3(aq) \longrightarrow \text{AgCl}(s) + \text{NaNO}_3(aq)$

Exercise:**Problem:**

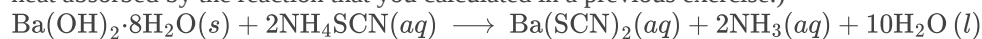
Calculate the enthalpy of solution (ΔH for the dissolution) per mole of NH_4NO_3 under the conditions described in [\[link\]](#).

Solution:

$$25 \text{ kJ mol}^{-1}$$

Exercise:**Problem:**

Calculate ΔH for the reaction described by the equation. (*Hint: use the value for the approximate amount of heat absorbed by the reaction that you calculated in a previous exercise.*)

**Exercise:**

Problem: Calculate the enthalpy of solution (ΔH for the dissolution) per mole of CaCl_2 (refer to exercise 25).

Solution:

$$81 \text{ kJ mol}^{-1}$$

Exercise:**Problem:**

Although the gas used in an oxyacetylene torch ([\[link\]](#)) is essentially pure acetylene, the heat produced by combustion of one mole of acetylene in such a torch is likely not equal to the enthalpy of combustion of acetylene listed in [\[link\]](#). Considering the conditions for which the tabulated data are reported, suggest an explanation.

Exercise:

Problem: How much heat is produced by burning 4.00 moles of acetylene under standard state conditions?

Solution:

$$5204.4 \text{ kJ}$$

Exercise:

Problem: How much heat is produced by combustion of 125 g of methanol under standard state conditions?

Exercise:**Problem:**

How many moles of isooctane must be burned to produce 100 kJ of heat under standard state conditions?

Solution:

$$1.83 \times 10^{-2} \text{ mol}$$

Exercise:**Problem:**

What mass of carbon monoxide must be burned to produce 175 kJ of heat under standard state conditions?

Exercise:**Problem:**

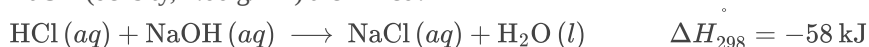
When 2.50 g of methane burns in oxygen, 125 kJ of heat is produced. What is the enthalpy of combustion per mole of methane under these conditions?

Solution:

$$-802 \text{ kJ mol}^{-1}$$

Exercise:**Problem:**

How much heat is produced when 100 mL of 0.250 M HCl (density, 1.00 g/mL) and 200 mL of 0.150 M NaOH (density, 1.00 g/mL) are mixed?



If both solutions are at the same temperature and the heat capacity of the products is 4.19 J/g °C, how much will the temperature increase? What assumption did you make in your calculation?

Exercise:**Problem:**

A sample of 0.562 g of carbon is burned in oxygen in a bomb calorimeter, producing carbon dioxide. Assume both the reactants and products are under standard state conditions, and that the heat released is directly proportional to the enthalpy of combustion of graphite. The temperature of the calorimeter increases from 26.74 °C to 27.93 °C. What is the heat capacity of the calorimeter and its contents?

Solution:

$$15.5 \text{ kJ/}^{\circ}\text{C}$$

Exercise:**Problem:**

Before the introduction of chlorofluorocarbons, sulfur dioxide (enthalpy of vaporization, 6.00 kcal/mol) was used in household refrigerators. What mass of SO₂ must be evaporated to remove as much heat as evaporation of 1.00 kg of CCl₂F₂ (enthalpy of vaporization is 17.4 kJ/mol)?

The vaporization reactions for SO_2 and CCl_2F_2 are $\text{SO}_2(l) \longrightarrow \text{SO}_2(g)$ and $\text{CCl}_2\text{F}(l) \longrightarrow \text{CCl}_2\text{F}_2(g)$, respectively.

Exercise:

Problem:

Homes may be heated by pumping hot water through radiators. What mass of water will provide the same amount of heat when cooled from 95.0 to 35.0 °C, as the heat provided when 100 g of steam is cooled from 110 °C to 100 °C.

Solution:

7.43 g

Exercise:

Problem: Which of the enthalpies of combustion in [\[link\]](#) the table are also standard enthalpies of formation?

Exercise:

Problem:

Does the standard enthalpy of formation of $\text{H}_2\text{O}(g)$ differ from ΔH° for the reaction $2\text{H}_2(g) + \text{O}_2(g) \longrightarrow 2\text{H}_2\text{O}(g)$?

Solution:

Yes.

Exercise:

Problem:

Joseph Priestly prepared oxygen in 1774 by heating red mercury(II) oxide with sunlight focused through a lens. How much heat is required to decompose exactly 1 mole of red $\text{HgO}(s)$ to $\text{Hg}(l)$ and $\text{O}_2(g)$ under standard conditions?

Exercise:

Problem:

How many kilojoules of heat will be released when exactly 1 mole of manganese, Mn, is burned to form $\text{Mn}_3\text{O}_4(s)$ at standard state conditions?

Solution:

459.6 kJ

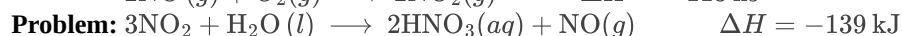
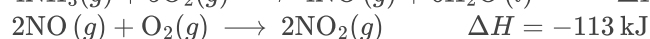
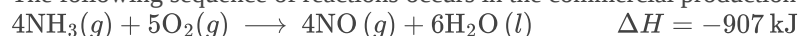
Exercise:

Problem:

How many kilojoules of heat will be released when exactly 1 mole of iron, Fe, is burned to form $\text{Fe}_2\text{O}_3(s)$ at standard state conditions?

Exercise:

The following sequence of reactions occurs in the commercial production of aqueous nitric acid:



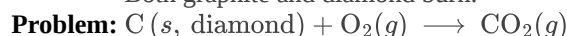
Determine the total energy change for the production of one mole of aqueous nitric acid by this process.

Solution:

−495 kJ/mol

Exercise:

Both graphite and diamond burn.



For the conversion of graphite to diamond:



Which produces more heat, the combustion of graphite or the combustion of diamond?

Exercise:

Problem:

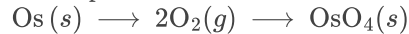
From the molar heats of formation in [Appendix G](#), determine how much heat is required to evaporate one mole of water: $\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g)$

Solution:

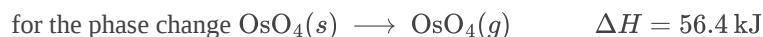
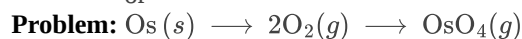
44.01 kJ/mol

Exercise:

Which produces more heat?

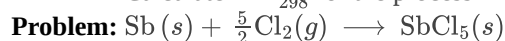


or

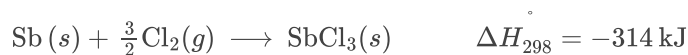


Exercise:

Calculate ΔH_{298}° for the process



from the following information:



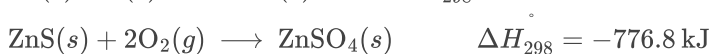
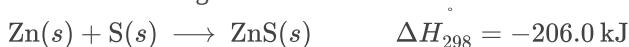
Solution:

−394 kJ

Exercise:



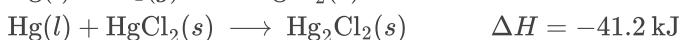
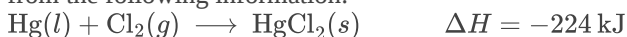
from the following information:



Exercise:

Problem: Calculate ΔH for the process $\text{Hg}_2\text{Cl}_2(s) \longrightarrow 2\text{Hg}(l) + \text{Cl}_2(g)$

from the following information:



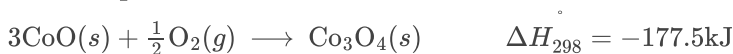
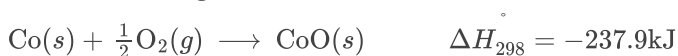
Solution:

265 kJ

Exercise:

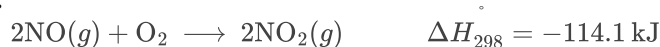
Problem: Calculate ΔH_{298}° for the process $\text{Co}_3\text{O}_4(s) \longrightarrow 3\text{Co}(s) + 2\text{O}_2(g)$

from the following information:



Exercise:

Calculate the standard molar enthalpy of formation of $\text{NO}(g)$ from the following data:



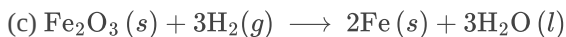
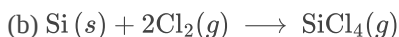
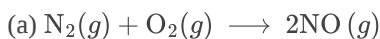
Solution:

90.3 kJ/mol

Exercise:

Problem:

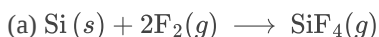
Using the data in [Appendix G](#), calculate the standard enthalpy change for each of the following reactions:

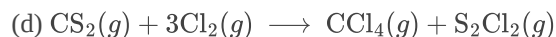
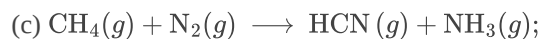
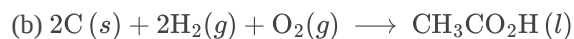


Exercise:

Problem:

Using the data in [Appendix G](#), calculate the standard enthalpy change for each of the following reactions:





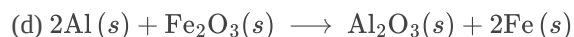
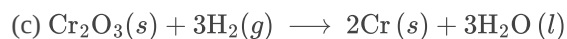
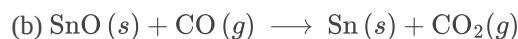
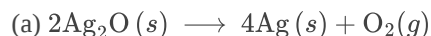
Solution:

(a) $-1615.0 \text{ kJ mol}^{-1}$; (b) $-484.3 \text{ kJ mol}^{-1}$; (c) 164.2 kJ ; (d) -232.1 kJ

Exercise:

Problem:

The following reactions can be used to prepare samples of metals. Determine the enthalpy change under standard state conditions for each.



Exercise:

Problem:

The decomposition of hydrogen peroxide, H_2O_2 , has been used to provide thrust in the control jets of various space vehicles. Using the data in [Appendix G](#), determine how much heat is produced by the decomposition of exactly 1 mole of H_2O_2 under standard conditions.



Solution:

$-54.04 \text{ kJ mol}^{-1}$

Exercise:

Problem:

Calculate the enthalpy of combustion of propane, $C_3H_8(g)$, for the formation of $H_2O(g)$ and $CO_2(g)$. The enthalpy of formation of propane is -104 kJ/mol .

Exercise:

Problem:

Calculate the enthalpy of combustion of butane, $C_4H_{10}(g)$ for the formation of $H_2O(g)$ and $CO_2(g)$. The enthalpy of formation of butane is -126 kJ/mol .

Solution:

$-2660 \text{ kJ mol}^{-1}$

Exercise:

Problem:

Both propane and butane are used as gaseous fuels. Which compound produces more heat per gram when burned?

Exercise:**Problem:**

The white pigment TiO_2 is prepared by the reaction of titanium tetrachloride, TiCl_4 , with water vapor in the gas phase: $\text{TiCl}_4(g) + 2\text{H}_2\text{O}(g) \longrightarrow \text{TiO}_2(s) + 4\text{HCl}(g)$.

How much heat is evolved in the production of exactly 1 mole of $\text{TiO}_2(s)$ under standard state conditions?

Solution:

67.1 kJ

Exercise:**Problem:**

Water gas, a mixture of H_2 and CO , is an important industrial fuel produced by the reaction of steam with red hot coke, essentially pure carbon: $\text{C}(s) + \text{H}_2\text{O}(g) \longrightarrow \text{CO}(g) + \text{H}_2(g)$.

(a) Assuming that coke has the same enthalpy of formation as graphite, calculate ΔH_{298}° for this reaction.

(b) Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and additional hydrogen at high temperature and pressure in the presence of a suitable catalyst:
 $2\text{H}_2(g) + \text{CO}(g) \longrightarrow \text{CH}_3\text{OH}(g)$.

Under the conditions of the reaction, methanol forms as a gas. Calculate ΔH_{298}° for this reaction and for the condensation of gaseous methanol to liquid methanol.

(c) Calculate the heat of combustion of 1 mole of liquid methanol to $\text{H}_2\text{O}(g)$ and $\text{CO}_2(g)$.

Exercise:**Problem:**

In the early days of automobiles, illumination at night was provided by burning acetylene, C_2H_2 . Though no longer used as auto headlamps, acetylene is still used as a source of light by some cave explorers. The acetylene is (was) prepared in the lamp by the reaction of water with calcium carbide, CaC_2 :
 $\text{CaC}_2(s) + 2\text{H}_2\text{O}(l) \longrightarrow \text{Ca}(\text{OH})_2(s) + \text{C}_2\text{H}_2(g)$.

Calculate the standard enthalpy of the reaction. The ΔH_f° of CaC_2 is -15.14 kcal/mol .

Solution:

-122.8 kJ

Exercise:**Problem:**

From the data in [\[link\]](#), determine which of the following fuels produces the greatest amount of heat per gram when burned under standard conditions: $\text{CO}(g)$, $\text{CH}_4(g)$, or $\text{C}_2\text{H}_2(g)$.

Exercise:**Problem:**

The enthalpy of combustion of hard coal averages -35 kJ/g , that of gasoline, $1.28 \times 10^5 \text{ kJ/gal}$. How many kilograms of hard coal provide the same amount of heat as is available from 1.0 gallon of gasoline? Assume that the density of gasoline is 0.692 g/mL (the same as the density of isooctane).

Solution:

3.7 kg

Exercise:

Problem: Ethanol, $\text{C}_2\text{H}_5\text{OH}$, is used as a fuel for motor vehicles, particularly in Brazil.

(a) Write the balanced equation for the combustion of ethanol to $\text{CO}_2(g)$ and $\text{H}_2\text{O}(g)$, and, using the data in [Appendix G](#), calculate the enthalpy of combustion of 1 mole of ethanol.

(b) The density of ethanol is 0.7893 g/mL. Calculate the enthalpy of combustion of exactly 1 L of ethanol.

(c) Assuming that an automobile's mileage is directly proportional to the heat of combustion of the fuel, calculate how much farther an automobile could be expected to travel on 1 L of gasoline than on 1 L of ethanol. Assume that gasoline has the heat of combustion and the density of n-octane, C_8H_{18}

($\Delta H_f^\circ = -208.4 \text{ kJ/mol}$; density = 0.7025 g/mL).

Exercise:

Problem:

Among the substances that react with oxygen and that have been considered as potential rocket fuels are diborane [B_2H_6 , produces $\text{B}_2\text{O}_3(s)$ and $\text{H}_2\text{O}(g)$], methane [CH_4 , produces $\text{CO}_2(g)$ and $\text{H}_2\text{O}(g)$], and hydrazine [N_2H_4 , produces $\text{N}_2(g)$ and $\text{H}_2\text{O}(g)$]. On the basis of the heat released by 1.00 g of each substance in its reaction with oxygen, which of these compounds offers the best possibility as a rocket fuel? The ΔH_f° of $\text{B}_2\text{H}_6(g)$, $\text{CH}_4(g)$, and $\text{N}_2\text{H}_4(l)$ may be found in [Appendix G](#).

Solution:

On the assumption that the best rocket fuel is the one that gives off the most heat, B_2H_6 is the prime candidate.

Exercise:

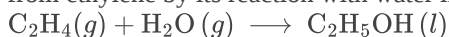
Problem:

How much heat is produced when 1.25 g of chromium metal reacts with oxygen gas under standard conditions?

Exercise:

Problem:

Ethylene, C_2H_4 , a byproduct from the fractional distillation of petroleum, is fourth among the 50 chemical compounds produced commercially in the largest quantities. About 80% of synthetic ethanol is manufactured from ethylene by its reaction with water in the presence of a suitable catalyst.



Using the data in the table in [Appendix G](#), calculate ΔH° for the reaction.

Solution:

-88.2 kJ

Exercise:

The oxidation of the sugar glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, is described by the following equation:



The metabolism of glucose gives the same products, although the glucose reacts with oxygen in a series of steps in the body.

(a) How much heat in kilojoules can be produced by the metabolism of 1.0 g of glucose?

(b) How many Calories can be produced by the metabolism of 1.0 g of glucose?

Exercise:

Problem: Propane, C_3H_8 , is a hydrocarbon that is commonly used as a fuel.

(a) Write a balanced equation for the complete combustion of propane gas.

(b) Calculate the volume of air at 25 °C and 1.00 atmosphere that is needed to completely combust 25.0 grams of propane. Assume that air is 21.0 percent O_2 by volume. (Hint: we will see how to do this calculation in a later chapter on gases—for now use the information that 1.00 L of air at 25 °C and 1.00 atm contains 0.275 g of O_2 per liter.)

(c) The heat of combustion of propane is $-2,219.2 \text{ kJ/mol}$. Calculate the heat of formation, ΔH_f° of propane given that ΔH_f° of $\text{H}_2\text{O}(l) = -285.8 \text{ kJ/mol}$ and ΔH_f° of $\text{CO}_2(g) = -393.5 \text{ kJ/mol}$.

(d) Assuming that all of the heat released in burning 25.0 grams of propane is transferred to 4.00 kilograms of water, calculate the increase in temperature of the water.

Solution:

(a) $\text{C}_3\text{H}_8(g) + 5\text{O}_2(g) \rightarrow 3\text{CO}_2(g) + 4\text{H}_2\text{O}(l)$; (b) 330 L; (c) $-104.5 \text{ kJ mol}^{-1}$; (d) 75.4 °C

Exercise:

Problem:

During a recent winter month in Sheboygan, Wisconsin, it was necessary to obtain 3500 kWh of heat provided by a natural gas furnace with 89% efficiency to keep a small house warm (the efficiency of a gas furnace is the percent of the heat produced by combustion that is transferred into the house).

(a) Assume that natural gas is pure methane and determine the volume of natural gas in cubic feet that was required to heat the house. The average temperature of the natural gas was 56 °F; at this temperature and a pressure of 1 atm, natural gas has a density of 0.681 g/L.

(b) How many gallons of LPG (liquefied petroleum gas) would be required to replace the natural gas used? Assume the LPG is liquid propane [C_3H_8 ; density, 0.5318 g/mL; enthalpy of combustion, 2219 kJ/mol for the formation of $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$] and the furnace used to burn the LPG has the same efficiency as the gas furnace.

(c) What mass of carbon dioxide is produced by combustion of the methane used to heat the house?

(d) What mass of water is produced by combustion of the methane used to heat the house?

(e) What volume of air is required to provide the oxygen for the combustion of the methane used to heat the house? Air contains 23% oxygen by mass. The average density of air during the month was 1.22 g/L.

(f) How many kilowatt-hours ($1 \text{ kWh} = 3.6 \times 10^6 \text{ J}$) of electricity would be required to provide the heat necessary to heat the house? Note electricity is 100% efficient in producing heat inside a house.

(g) Although electricity is 100% efficient in producing heat inside a house, production and distribution of electricity is not 100% efficient. The efficiency of production and distribution of electricity produced in a coal-fired power plant is about 40%. A certain type of coal provides 2.26 kWh per pound upon combustion. What mass of this coal in kilograms will be required to produce the electrical energy necessary to heat the house if the efficiency of generation and distribution is 40%?

Glossary

chemical thermodynamics

area of science that deals with the relationships between heat, work, and all forms of energy associated with chemical and physical processes

enthalpy (H)

sum of a system's internal energy and the mathematical product of its pressure and volume

enthalpy change (ΔH)

heat released or absorbed by a system under constant pressure during a chemical or physical process

expansion work (pressure-volume work)

work done as a system expands or contracts against external pressure

first law of thermodynamics

internal energy of a system changes due to heat flow in or out of the system or work done on or by the system

Hess's law

if a process can be represented as the sum of several steps, the enthalpy change of the process equals the sum of the enthalpy changes of the steps

hydrocarbon

compound composed only of hydrogen and carbon; the major component of fossil fuels

internal energy (U)

total of all possible kinds of energy present in a substance or substances

standard enthalpy of combustion (ΔH_c°)

heat released when one mole of a compound undergoes complete combustion under standard conditions

standard enthalpy of formation (ΔH_f°)

enthalpy change of a chemical reaction in which 1 mole of a pure substance is formed from its elements in their most stable states under standard state conditions

standard state

set of physical conditions as accepted as common reference conditions for reporting thermodynamic properties; 1 bar of pressure, and solutions at 1 molar concentrations, usually at a temperature of 298.15 K

state function

property depending only on the state of a system, and not the path taken to reach that state

Introduction

class="introduction"

- Intermolecular Forces
- Properties of Liquids
- Phase Transitions
- Phase Diagrams
- The Solid State of Matter
- Lattice Structures in Crystalline Solids

Solid carbon
dioxide

("dry ice",
left)

sublimes
vigorously
when placed
in a liquid
(right),
cooling the
liquid and
generating a
fog of
condensed
water vapor
above the
cylinder.
(credit:
modificatio
n of work
by Paul
Flowers)



The great distances between atoms and molecules in a gaseous phase, and the corresponding absence of any significant interactions between them, allows for simple descriptions of many physical properties that are the same for all gases, regardless of their chemical identities. As described in the final module of the chapter on gases, this situation changes at high pressures and low temperatures—conditions that permit the atoms and molecules to interact to a much greater extent. In the liquid and solid states, these interactions are of considerable strength and play an important role in determining a number of physical properties that *do* depend on the chemical identity of the substance. In this chapter, the nature of these interactions and their effects on various physical properties of liquid and solid phases will be examined.

The Kinetic-Molecular Theory

- State the postulates of the kinetic-molecular theory
- Use this theory's postulates to explain the gas laws

The gas laws that we have seen to this point, as well as the ideal gas equation, are empirical, that is, they have been derived from experimental observations. The mathematical forms of these laws closely describe the macroscopic behavior of most gases at pressures less than about 1 or 2 atm. Although the gas laws describe relationships that have been verified by many experiments, they do not tell us why gases follow these relationships.

The **kinetic molecular theory** (KMT) is a simple microscopic model that effectively explains the gas laws described in previous modules of this chapter. This theory is based on the following five postulates described here. (Note: The term “molecule” will be used to refer to the individual chemical species that compose the gas, although some gases are composed of atomic species, for example, the noble gases.)

1. Gases are composed of molecules that are in continuous motion, travelling in straight lines and changing direction only when they collide with other molecules or with the walls of a container.
2. The molecules composing the gas are negligibly small compared to the distances between them.
3. The pressure exerted by a gas in a container results from collisions between the gas molecules and the container walls.
4. Gas molecules exert no attractive or repulsive forces on each other or the container walls; therefore, their collisions are *elastic* (do not involve a loss of energy).
5. The average kinetic energy of the gas molecules is proportional to the kelvin temperature of the gas.

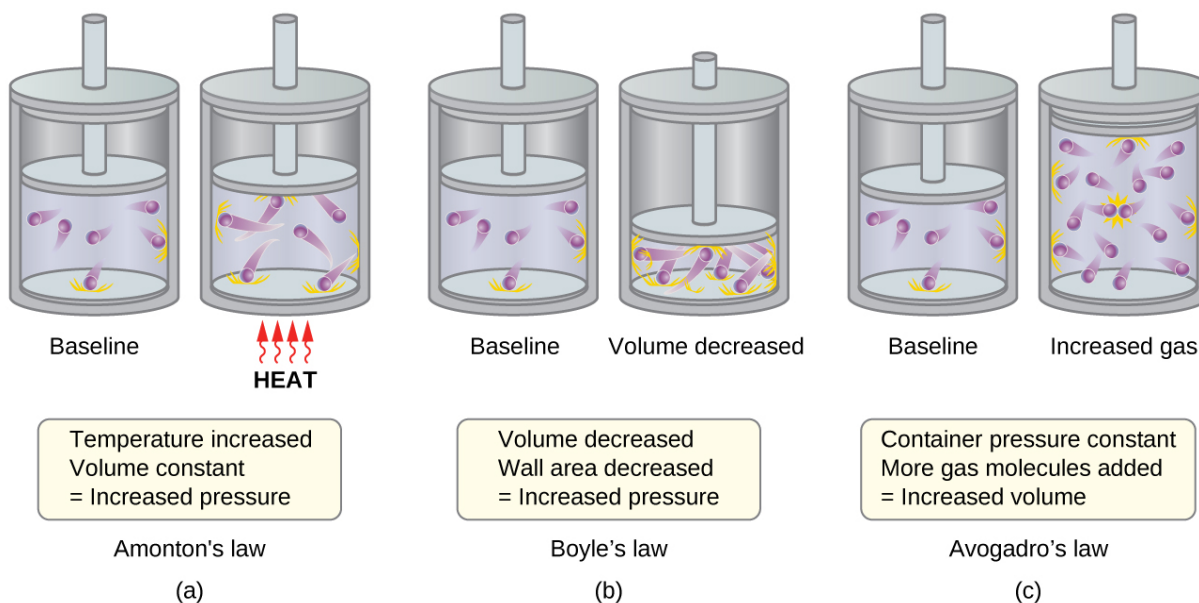
The test of the KMT and its postulates is its ability to explain and describe the behavior of a gas. The various gas laws can be derived from the assumptions of the KMT, which have led chemists to believe that the assumptions of the theory accurately represent the properties of gas molecules. We will first look at the individual gas laws (Boyle's, Charles's, Amontons's, Avogadro's, and Dalton's laws) conceptually to see how the KMT explains them. Then, we will more

carefully consider the relationships between molecular masses, speeds, and kinetic energies with temperature, and explain Graham's law.

The Kinetic-Molecular Theory Explains the Behavior of Gases, Part I

Recalling that gas pressure is exerted by rapidly moving gas molecules and depends directly on the number of molecules hitting a unit area of the wall per unit of time, we see that the KMT conceptually explains the behavior of a gas as follows:

- *Amontons's law.* If the temperature is increased, the average speed and kinetic energy of the gas molecules increase. If the volume is held constant, the increased speed of the gas molecules results in more frequent and more forceful collisions with the walls of the container, therefore increasing the pressure ([\[link\]](#)).
- *Charles's law.* If the temperature of a gas is increased, a constant pressure may be maintained only if the volume occupied by the gas increases. This will result in greater average distances traveled by the molecules to reach the container walls, as well as increased wall surface area. These conditions will decrease both the frequency of molecule-wall collisions and the number of collisions per unit area, the combined effects of which balance the effect of increased collision forces due to the greater kinetic energy at the higher temperature.
- *Boyle's law.* If the gas volume is decreased, the container wall area decreases and the molecule-wall collision frequency increases, both of which increase the pressure exerted by the gas ([\[link\]](#)).
- *Avogadro's law.* At constant pressure and temperature, the frequency and force of molecule-wall collisions are constant. Under such conditions, increasing the number of gaseous molecules will require a proportional increase in the container volume in order to yield a decrease in the number of collisions per unit area to compensate for the increased frequency of collisions ([\[link\]](#)).
- *Dalton's Law.* Because of the large distances between them, the molecules of one gas in a mixture bombard the container walls with the same frequency whether other gases are present or not, and the total pressure of a gas mixture equals the sum of the (partial) pressures of the individual gases.

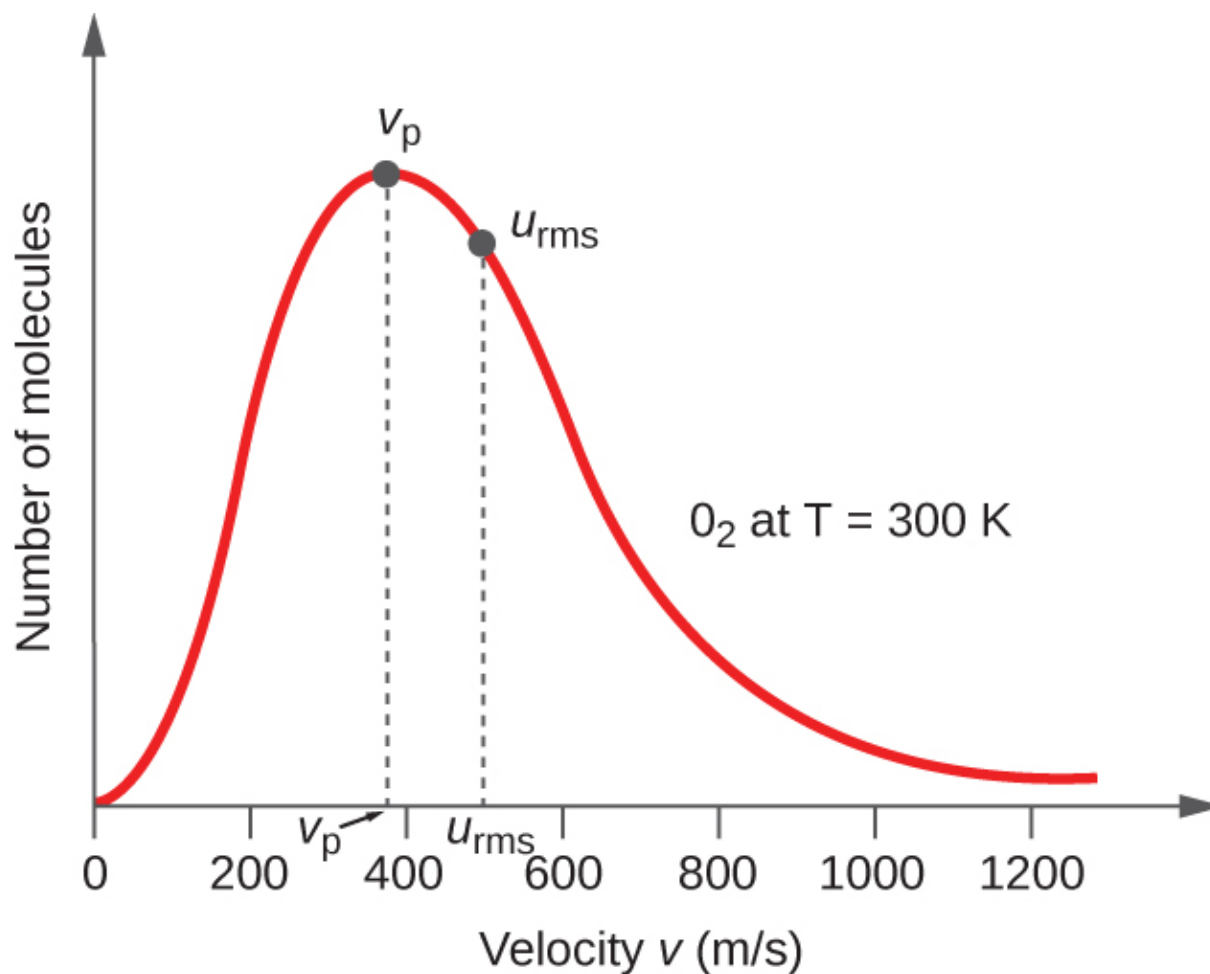


(a) When gas temperature increases, gas pressure increases due to increased force and frequency of molecular collisions. (b) When volume decreases, gas pressure increases due to increased frequency of molecular collisions. (c) When the amount of gas increases at a constant pressure, volume increases to yield a constant number of collisions per unit wall area per unit time.

Molecular Velocities and Kinetic Energy

The previous discussion showed that the KMT qualitatively explains the behaviors described by the various gas laws. The postulates of this theory may be applied in a more quantitative fashion to derive these individual laws. To do this, we must first look at velocities and kinetic energies of gas molecules, and the temperature of a gas sample.

In a gas sample, individual molecules have widely varying speeds; however, because of the *vast* number of molecules and collisions involved, the molecular speed distribution and average speed are constant. This molecular speed distribution is known as a Maxwell-Boltzmann distribution, and it depicts the relative numbers of molecules in a bulk sample of gas that possesses a given speed ([link](#)).



The molecular speed distribution for oxygen gas at 300 K is shown here.

Very few molecules move at either very low or very high speeds. The number of molecules with intermediate speeds increases rapidly up to a maximum, which is the most probable speed, then drops off rapidly. Note that the most probable speed, v_p , is a little less than 400 m/s, while the root mean square speed, u_{rms} , is closer to 500 m/s.

The kinetic energy (KE) of a particle of mass (m) and speed (u) is given by:

Equation:

$$KE = \frac{1}{2} mu^2$$

Expressing mass in kilograms and speed in meters per second will yield energy values in units of joules ($J = \text{kg m}^2 \text{s}^{-2}$). To deal with a large number of gas molecules, we use averages for both speed and kinetic energy. In the KMT, the **root mean square velocity** of a particle, u_{rms} , is defined as the square root of the average of the squares of the velocities with n = the number of particles:

Equation:

$$u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + u_4^2 + \dots}{n}}$$

The average kinetic energy for a mole of particles, KE_{avg} , is then equal to:

Equation:

$$\text{KE}_{\text{avg}} = \frac{1}{2} M u_{\text{rms}}^2$$

The KE_{avg} of a mole of gas molecules is also directly proportional to the temperature of the gas and may be described by the equation:

Equation:

$$\text{KE}_{\text{avg}} = \frac{3}{2} RT$$

where R is the gas constant and T is the kelvin temperature. When used in this equation, the appropriate form of the gas constant is $8.314 \text{ J/mol}\cdot\text{K}$ ($8.314 \text{ kg m}^2\text{s}^{-2}\text{mol}^{-1}\text{K}^{-1}$). These two separate equations for KE_{avg} may be combined and rearranged to yield a relation between molecular speed and temperature:

Equation:

$$\frac{1}{2} M u_{\text{rms}}^2 = \frac{3}{2} RT$$

Equation:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

Example:**Calculation of u_{rms}**

Calculate the root-mean-square velocity for a nitrogen molecule at 30 °C.

Solution

Convert the temperature into Kelvin:

Equation:

$$30\text{ }^{\circ}\text{C} + 273 = 303\text{ K}$$

Determine the molar mass of nitrogen in kilograms:

Equation:

$$\frac{28.0\text{ g}}{1\text{ mol}} \times \frac{1\text{ kg}}{1000\text{ g}} = 0.028\text{ kg/mol}$$

Replace the variables and constants in the root-mean-square velocity equation, replacing Joules with the equivalent $\text{kg m}^2\text{s}^{-2}$:

Equation:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{m}}$$

Equation:

$$u_{\text{rms}} = \sqrt{\frac{3(8.314\text{ J/mol K})(303\text{ K})}{(0.028\text{ kg/mol})}} = \sqrt{2.70 \times 10^5\text{ m}^2\text{s}^{-2}} = 519\text{ m/s}$$

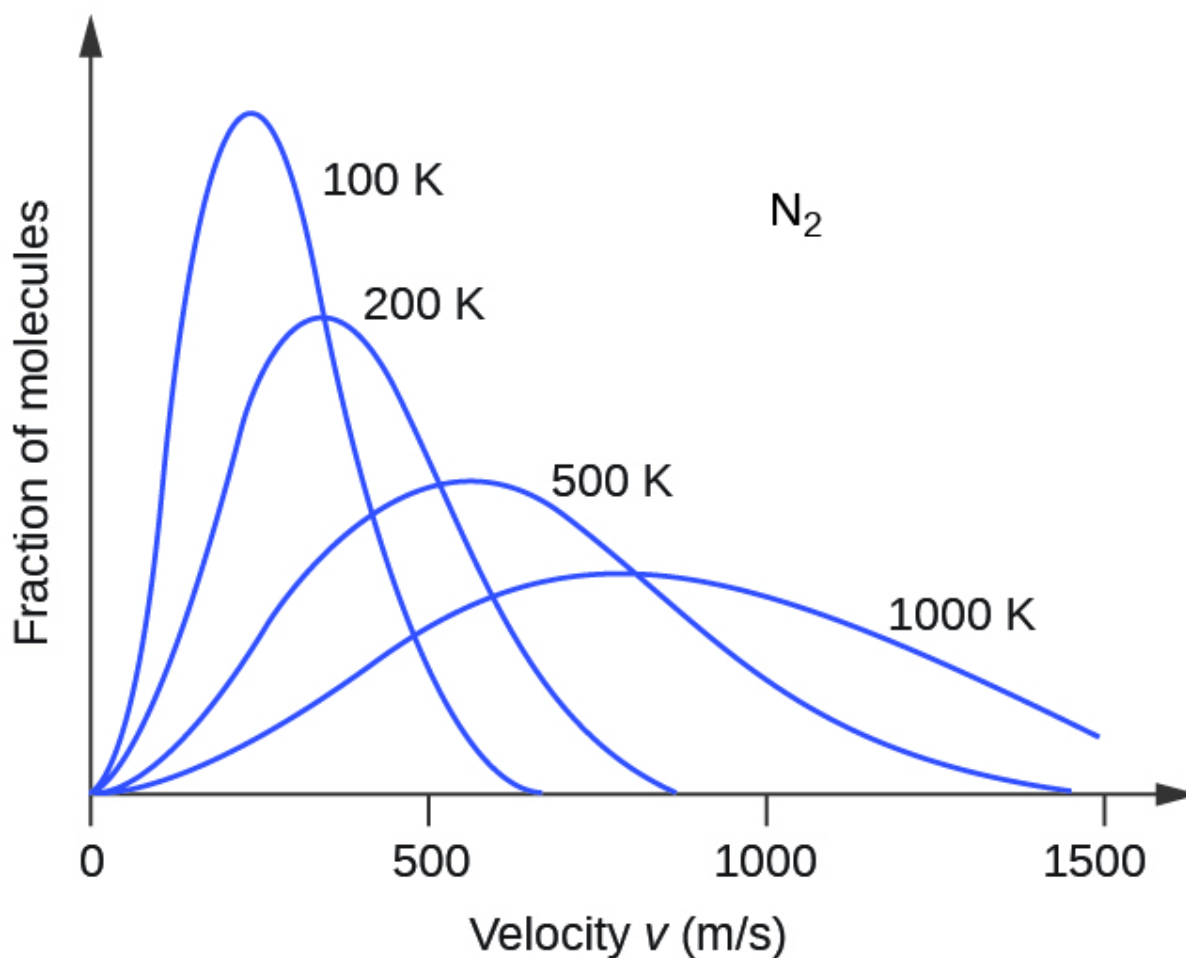
Check Your Learning

Calculate the root-mean-square velocity for a mole of oxygen molecules at – 23 °C.

Note:**Answer:**

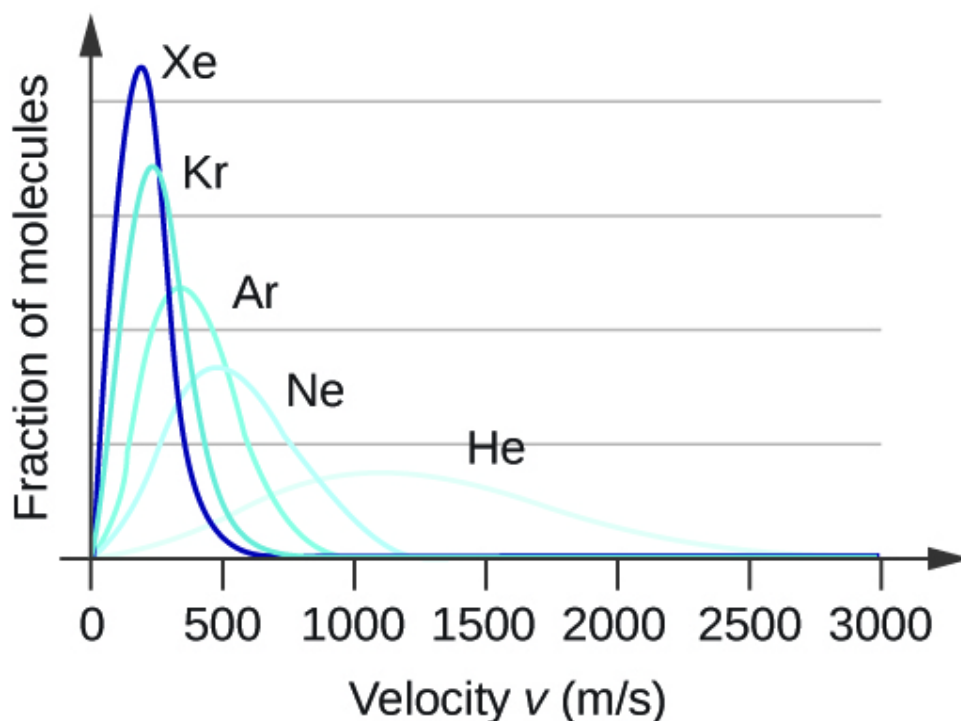
441 m/s

If the temperature of a gas increases, its KE_{avg} increases, more molecules have higher speeds and fewer molecules have lower speeds, and the distribution shifts toward higher speeds overall, that is, to the right. If temperature decreases, KE_{avg} decreases, more molecules have lower speeds and fewer molecules have higher speeds, and the distribution shifts toward lower speeds overall, that is, to the left. This behavior is illustrated for nitrogen gas in [\[link\]](#).



The molecular speed distribution for nitrogen gas (N_2) shifts to the right and flattens as the temperature increases; it shifts to the left and heightens as the temperature decreases.

At a given temperature, all gases have the same KE_{avg} for their molecules. Gases composed of lighter molecules have more high-speed particles and a higher u_{rms} , with a speed distribution that peaks at relatively higher velocities. Gases consisting of heavier molecules have more low-speed particles, a lower u_{rms} , and a speed distribution that peaks at relatively lower velocities. This trend is demonstrated by the data for a series of noble gases shown in [\[link\]](#).



Molecular velocity is directly related to molecular mass. At a given temperature, lighter molecules move faster on average than heavier molecules.

Note:



The [gas simulator](#) may be used to examine the effect of temperature on molecular velocities. Examine the simulator's "energy histograms" (molecular speed distributions) and "species information" (which gives average speed values) for molecules of different masses at various temperatures.

The Kinetic-Molecular Theory Explains the Behavior of Gases, Part II

According to Graham's law, the molecules of a gas are in rapid motion and the molecules themselves are small. The average distance between the molecules of a gas is large compared to the size of the molecules. As a consequence, gas molecules can move past each other easily and diffuse at relatively fast rates.

The rate of effusion of a gas depends directly on the (average) speed of its molecules:

Equation:

$$\text{effusion rate} \propto u_{\text{rms}}$$

Using this relation, and the equation relating molecular speed to mass, Graham's law may be easily derived as shown here:

Equation:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

Equation:

$$M = \frac{3RT}{u_{\text{rms}}^2} = \frac{3RT}{\bar{u}^2}$$

Equation:

$$\frac{\text{effusion rate A}}{\text{effusion rate B}} = \frac{u_{\text{rms A}}}{u_{\text{rms B}}} = \frac{\sqrt{\frac{3RT}{M_{\text{A}}}}}{\sqrt{\frac{3RT}{M_{\text{B}}}}} = \sqrt{\frac{M_{\text{B}}}{M_{\text{A}}}}$$

The ratio of the rates of effusion is thus derived to be inversely proportional to the ratio of the square roots of their masses. This is the same relation observed experimentally and expressed as Graham's law.

Key Concepts and Summary

The kinetic molecular theory is a simple but very effective model that effectively explains ideal gas behavior. The theory assumes that gases consist of widely separated molecules of negligible volume that are in constant motion, colliding elastically with one another and the walls of their container with average velocities determined by their absolute temperatures. The individual molecules of a gas exhibit a range of velocities, the distribution of these velocities being dependent on the temperature of the gas and the mass of its molecules.

Key Equations

- $u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + u_4^2 + \dots}{n}}$
- $\text{KE}_{\text{avg}} = \frac{3}{2}RT$
- $u_{\text{rms}} = \sqrt{\frac{3RT}{m}}$

Chemistry End of Chapter Exercises

Exercise:

Problem:

Using the postulates of the kinetic molecular theory, explain why a gas uniformly fills a container of any shape.

Exercise:**Problem:**

Can the speed of a given molecule in a gas double at constant temperature? Explain your answer.

Solution:

Yes. At any given instant, there are a range of values of molecular speeds in a sample of gas. Any single molecule can speed up or slow down as it collides with other molecules. The average velocity of all the molecules is constant at constant temperature.

Exercise:**Problem:**

Describe what happens to the average kinetic energy of ideal gas molecules when the conditions are changed as follows:

- (a) The pressure of the gas is increased by reducing the volume at constant temperature.
- (b) The pressure of the gas is increased by increasing the temperature at constant volume.
- (c) The average velocity of the molecules is increased by a factor of 2.

Exercise:**Problem:**

The distribution of molecular velocities in a sample of helium is shown in [\[link\]](#). If the sample is cooled, will the distribution of velocities look more like that of H_2 or of H_2O ? Explain your answer.

Solution:

H₂O. Cooling slows the velocities of the He atoms, causing them to behave as though they were heavier.

Exercise:

Problem:

What is the ratio of the average kinetic energy of a SO₂ molecule to that of an O₂ molecule in a mixture of two gases? What is the ratio of the root mean square speeds, u_{rms} , of the two gases?

Exercise:

Problem:

A 1-L sample of CO initially at STP is heated to 546 K, and its volume is increased to 2 L.

- (a) What effect do these changes have on the number of collisions of the molecules of the gas per unit area of the container wall?
- (b) What is the effect on the average kinetic energy of the molecules?
- (c) What is the effect on the root mean square speed of the molecules?

Solution:

- (a) The number of collisions per unit area of the container wall is constant.
- (b) The average kinetic energy doubles. (c) The root mean square speed increases to $\sqrt{2}$ times its initial value; u_{rms} is proportional to $\sqrt{\text{KE}_{\text{avg}}}$.

Exercise:

Problem:

The root mean square speed of H₂ molecules at 25 °C is about 1.6 km/s. What is the root mean square speed of a N₂ molecule at 25 °C?

Exercise:

Problem: Answer the following questions:

- (a) Is the pressure of the gas in the hot air balloon shown at the opening of this chapter greater than, less than, or equal to that of the atmosphere outside the balloon?
- (b) Is the density of the gas in the hot air balloon shown at the opening of this chapter greater than, less than, or equal to that of the atmosphere outside the balloon?
- (c) At a pressure of 1 atm and a temperature of 20 °C, dry air has a density of 1.2256 g/L. What is the (average) molar mass of dry air?
- (d) The average temperature of the gas in a hot air balloon is 1.30×10^2 °F. Calculate its density, assuming the molar mass equals that of dry air.
- (e) The lifting capacity of a hot air balloon is equal to the difference in the mass of the cool air displaced by the balloon and the mass of the gas in the balloon. What is the difference in the mass of 1.00 L of the cool air in part (c) and the hot air in part (d)?
- (f) An average balloon has a diameter of 60 feet and a volume of 1.1×10^5 ft³. What is the lifting power of such a balloon? If the weight of the balloon and its rigging is 500 pounds, what is its capacity for carrying passengers and cargo?
- (g) A balloon carries 40.0 gallons of liquid propane (density 0.5005 g/L). What volume of CO₂ and H₂O gas is produced by the combustion of this propane?
- (h) A balloon flight can last about 90 minutes. If all of the fuel is burned during this time, what is the approximate rate of heat loss (in kJ/min) from the hot air in the bag during the flight?
-

Solution:

- (a) equal; (b) less than; (c) 29.48 g mol⁻¹; (d) 1.0966 g L⁻¹; (e) 0.129 g/L; (f) 4.01×10^5 g; net lifting capacity = 384 lb; (g) 270 L; (h) 39.1 kJ min⁻¹

Exercise:

Problem:

Show that the ratio of the rate of diffusion of Gas 1 to the rate of diffusion of Gas 2, $\frac{R_1}{R_2}$, is the same at 0 °C and 100 °C.

Glossary

kinetic molecular theory

theory based on simple principles and assumptions that effectively explains ideal gas behavior

root mean square velocity (u_{rms})

measure of average velocity for a group of particles calculated as the square root of the average squared velocity

Intermolecular Forces

By the end of this section, you will be able to:

- Describe the types of intermolecular forces possible between atoms or molecules in condensed phases (dispersion forces, dipole-dipole attractions, and hydrogen bonding)
- Identify the types of intermolecular forces experienced by specific molecules based on their structures
- Explain the relation between the intermolecular forces present within a substance and the temperatures associated with changes in its physical state

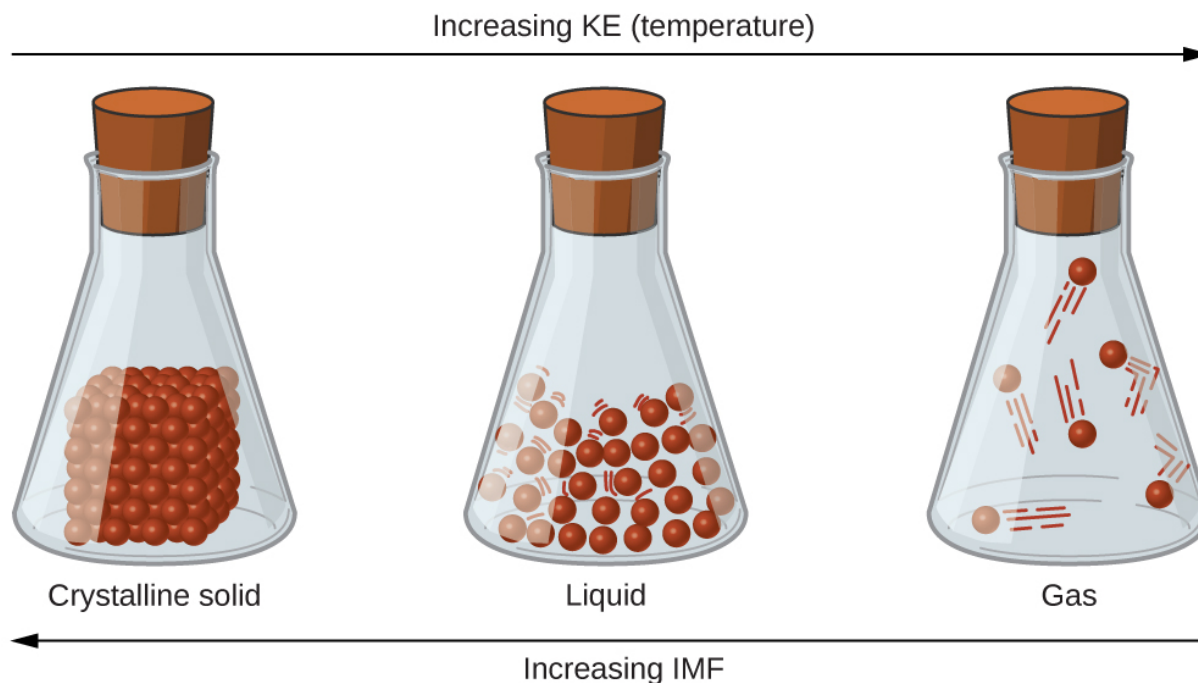
As was the case for gaseous substances, the kinetic molecular theory may be used to explain the behavior of solids and liquids. In the following description, the term *particle* will be used to refer to an atom, molecule, or ion. Note that we will use the popular phrase “intermolecular attraction” to refer to attractive forces between the particles of a substance, regardless of whether these particles are molecules, atoms, or ions.

Consider these two aspects of the molecular-level environments in solid, liquid, and gaseous matter:

- Particles in a solid are tightly packed together and often arranged in a regular pattern; in a liquid, they are close together with no regular arrangement; in a gas, they are far apart with no regular arrangement.
- Particles in a solid vibrate about fixed positions and do not generally move in relation to one another; in a liquid, they move past each other but remain in essentially constant contact; in a gas, they move independently of one another except when they collide.

The differences in the properties of a solid, liquid, or gas reflect the strengths of the attractive forces between the atoms, molecules, or ions that make up each phase. The phase in which a substance exists depends on the relative extents of its **intermolecular forces** (IMFs) and the kinetic energies (KE) of its molecules. IMFs are the various forces of attraction that may exist between the atoms and molecules of a substance due to electrostatic phenomena, as will be detailed in this module. These forces serve to hold particles close together, whereas the particles' KE provides the energy

required to overcome the attractive forces and thus increase the distance between particles. [\[link\]](#) illustrates how changes in physical state may be induced by changing the temperature, hence, the average KE, of a given substance.



Transitions between solid, liquid, and gaseous states of a substance occur when conditions of temperature or pressure favor the associated changes in intermolecular forces. (Note: The space between particles in the gas phase is much greater than shown.)

As an example of the processes depicted in this figure, consider a sample of water. When gaseous water is cooled sufficiently, the attractions between H_2O molecules will be capable of holding them together when they come into contact with each other; the gas condenses, forming liquid H_2O . For example, liquid water forms on the outside of a cold glass as the water vapor in the air is cooled by the cold glass, as seen in [\[link\]](#).



(a)



(b)

Condensation forms when water vapor in the air is cooled enough to form liquid water, such as (a) on the outside of a cold beverage glass or (b) in the form of fog. (credit a: modification of work by Jenny Downing; credit b: modification of work by Cory Zanker)

We can also liquefy many gases by compressing them, if the temperature is not too high. The increased pressure brings the molecules of a gas closer together, such that the attractions between the molecules become strong relative to their KE. Consequently, they form liquids. Butane, C_4H_{10} , is the fuel used in disposable lighters and is a gas at standard temperature and pressure. Inside the lighter's fuel compartment, the butane is compressed to a pressure that results in its condensation to the liquid state, as shown in [\[link\]](#).



Gaseous butane is compressed within the storage compartment of a disposable lighter, resulting in its condensation to the liquid state.
(credit: modification of work by "Sam-Cat"/Flickr)

Finally, if the temperature of a liquid becomes sufficiently low, or the pressure on the liquid becomes sufficiently high, the molecules of the liquid no longer have enough KE to overcome the IMF between them, and a solid forms. A more thorough discussion of these and other changes of state, or phase transitions, is provided in a later module of this chapter.

Note:

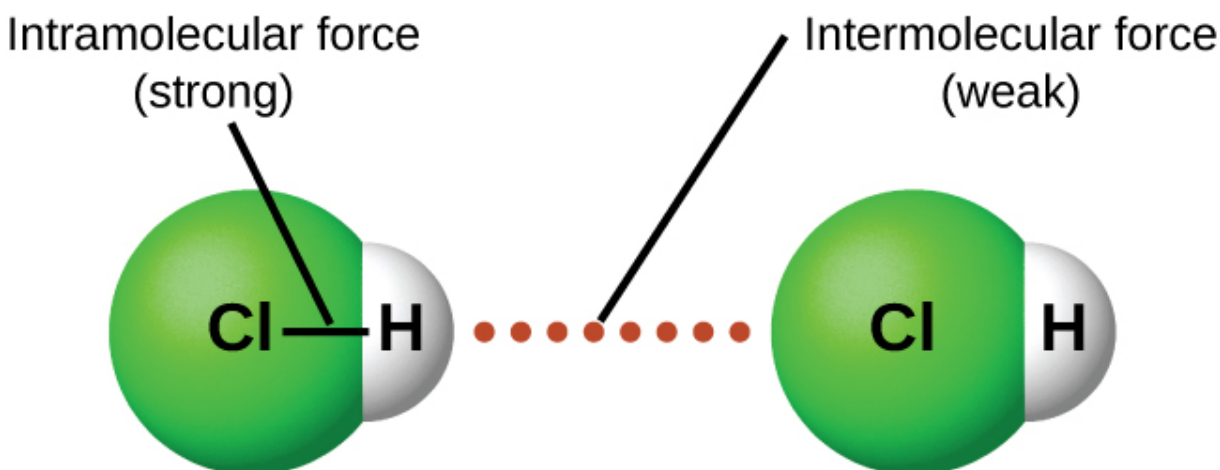


Access this [interactive simulation](#) on states of matter, phase transitions, and intermolecular forces. This simulation is useful for visualizing concepts introduced throughout this chapter.

Forces between Molecules

Under appropriate conditions, the attractions between all gas molecules will cause them to form liquids or solids. This is due to intermolecular forces, not *intramolecular* forces. *Intramolecular* forces are those *within* the molecule that keep the molecule together, for example, the bonds between the atoms. *Intermolecular* forces are the attractions *between* molecules, which determine many of the physical properties of a substance. [\[link\]](#) illustrates these different molecular forces. The strengths of these attractive forces vary widely, though usually the IMFs between small molecules are weak compared to the intramolecular forces that bond atoms together within a molecule. For example, to overcome the IMFs in one mole of

liquid HCl and convert it into gaseous HCl requires only about 17 kilojoules. However, to break the covalent bonds between the hydrogen and chlorine atoms in one mole of HCl requires about 25 times more energy—430 kilojoules.



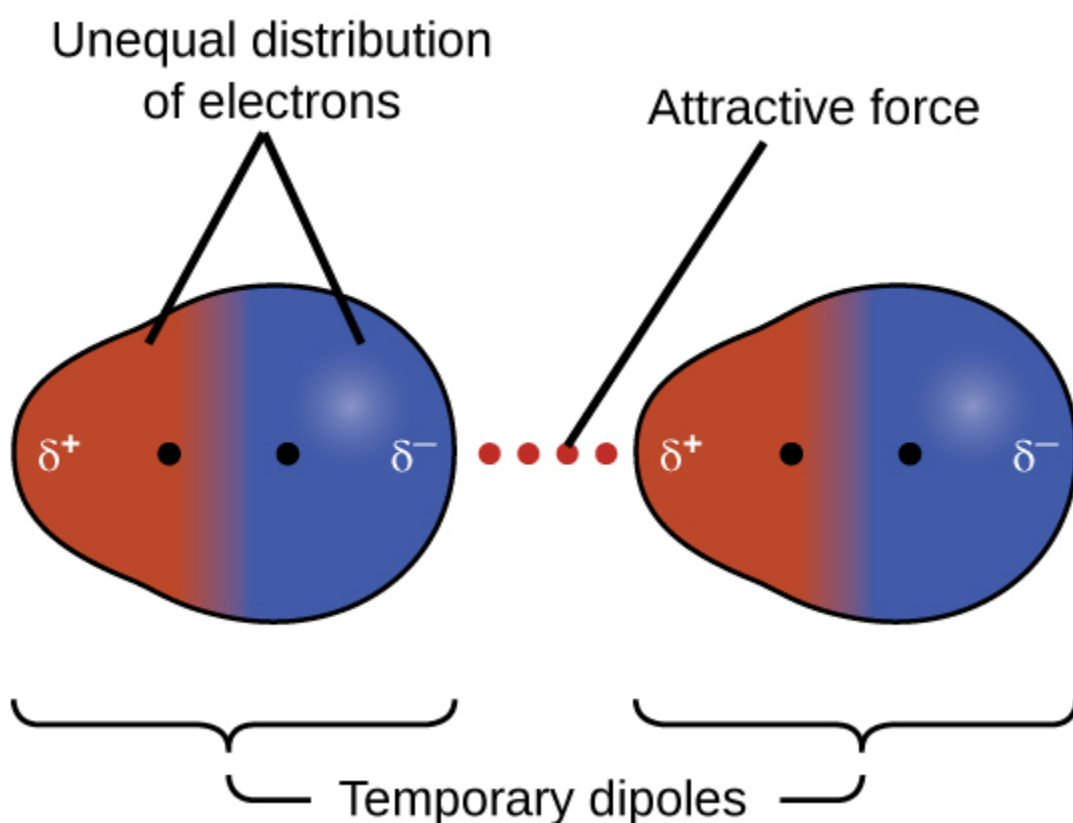
Intramolecular forces keep a molecule intact. *Intermolecular* forces hold multiple molecules together and determine many of a substance's properties.

All of the attractive forces between neutral atoms and molecules are known as **van der Waals forces**, although they are usually referred to more informally as intermolecular attraction. We will consider the various types of IMFs in the next three sections of this module.

Dispersion Forces

One of the three van der Waals forces is present in all condensed phases, regardless of the nature of the atoms or molecules composing the substance. This attractive force is called the London dispersion force in honor of German-born American physicist Fritz London who, in 1928, first explained it. This force is often referred to as simply the **dispersion force**. Because the electrons of an atom or molecule are in constant motion (or,

alternatively, the electron's location is subject to quantum-mechanical variability), at any moment in time, an atom or molecule can develop a temporary, **instantaneous dipole** if its electrons are distributed asymmetrically. The presence of this dipole can, in turn, distort the electrons of a neighboring atom or molecule, producing an **induced dipole**. These two rapidly fluctuating, temporary dipoles thus result in a relatively weak electrostatic attraction between the species—a so-called dispersion force like that illustrated in [\[link\]](#).



Dispersion forces result from the formation of temporary dipoles, as illustrated here for two nonpolar diatomic molecules.

Dispersion forces that develop between atoms in different molecules can attract the two molecules to each other. The forces are relatively weak,

however, and become significant only when the molecules are very close. Larger and heavier atoms and molecules exhibit stronger dispersion forces than do smaller and lighter atoms and molecules. F_2 and Cl_2 are gases at room temperature (reflecting weaker attractive forces); Br_2 is a liquid, and I_2 is a solid (reflecting stronger attractive forces). Trends in observed melting and boiling points for the halogens clearly demonstrate this effect, as seen in [\[link\]](#).

Melting and Boiling Points of the Halogens				
Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
fluorine, F_2	38 g/mol	72 pm	53 K	85 K
chlorine, Cl_2	71 g/mol	99 pm	172 K	238 K
bromine, Br_2	160 g/mol	114 pm	266 K	332 K
iodine, I_2	254 g/mol	133 pm	387 K	457 K
astatine, At_2	420 g/mol	150 pm	575 K	610 K

The increase in melting and boiling points with increasing atomic/molecular size may be rationalized by considering how the strength of dispersion forces is affected by the electronic structure of the atoms or molecules in the substance. In a larger atom, the valence electrons are, on average,

farther from the nuclei than in a smaller atom. Thus, they are less tightly held and can more easily form the temporary dipoles that produce the attraction. The measure of how easy or difficult it is for another electrostatic charge (for example, a nearby ion or polar molecule) to distort a molecule's charge distribution (its electron cloud) is known as **polarizability**. A molecule that has a charge cloud that is easily distorted is said to be very polarizable and will have large dispersion forces; one with a charge cloud that is difficult to distort is not very polarizable and will have small dispersion forces.

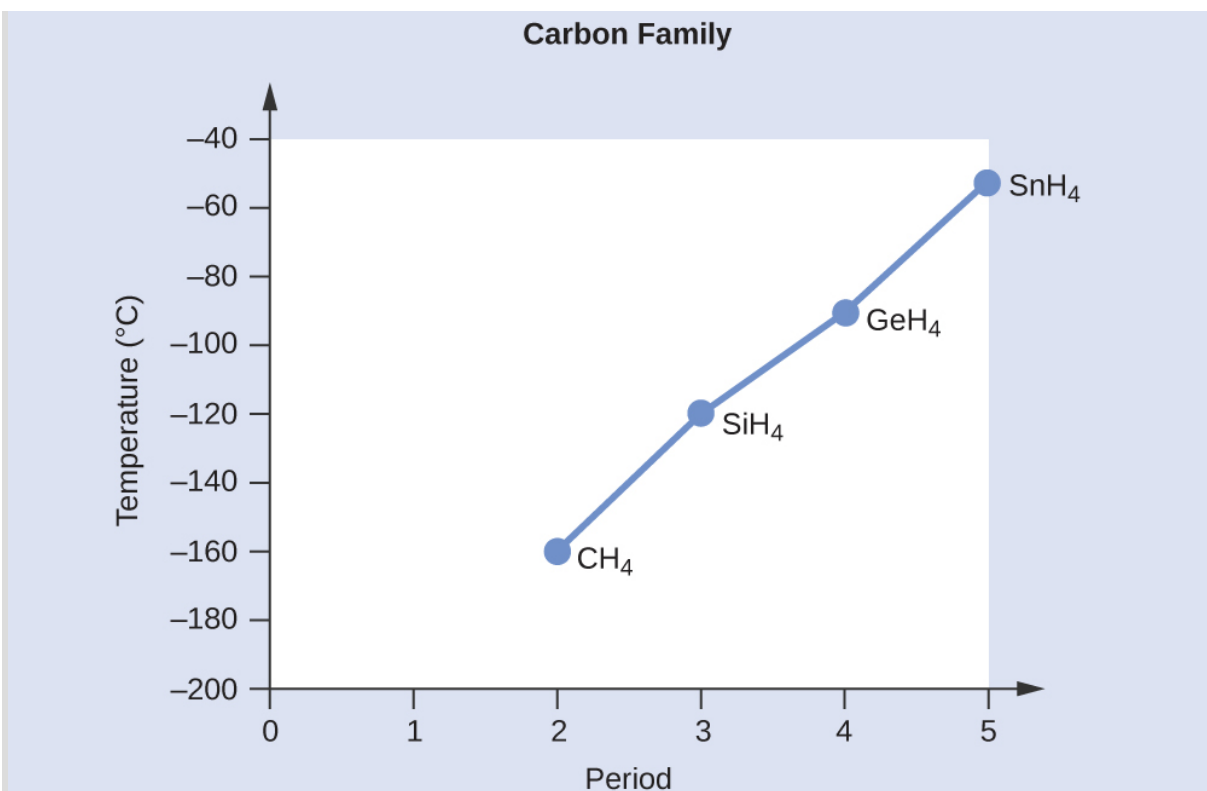
Example:**London Forces and Their Effects**

Order the following compounds of a group 14 element and hydrogen from lowest to highest boiling point: CH_4 , SiH_4 , GeH_4 , and SnH_4 . Explain your reasoning.

Solution

Applying the skills acquired in the chapter on chemical bonding and molecular geometry, all of these compounds are predicted to be nonpolar, so they may experience only dispersion forces: the smaller the molecule, the less polarizable and the weaker the dispersion forces; the larger the molecule, the larger the dispersion forces. The molar masses of CH_4 , SiH_4 , GeH_4 , and SnH_4 are approximately 16 g/mol, 32 g/mol, 77 g/mol, and 123 g/mol, respectively. Therefore, CH_4 is expected to have the lowest boiling point and SnH_4 the highest boiling point. The ordering from lowest to highest boiling point is expected to be $\text{CH}_4 < \text{SiH}_4 < \text{GeH}_4 < \text{SnH}_4$.

A graph of the actual boiling points of these compounds versus the period of the group 14 element shows this prediction to be correct:



Check Your Learning

Order the following hydrocarbons from lowest to highest boiling point: C₂H₆, C₃H₈, and C₄H₁₀.

Note:

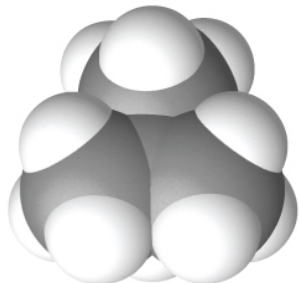
Answer:

C₂H₆ < C₃H₈ < C₄H₁₀. All of these compounds are nonpolar and only have London dispersion forces: the larger the molecule, the larger the dispersion forces and the higher the boiling point. The ordering from lowest to highest boiling point is therefore C₂H₆ < C₃H₈ < C₄H₁₀.

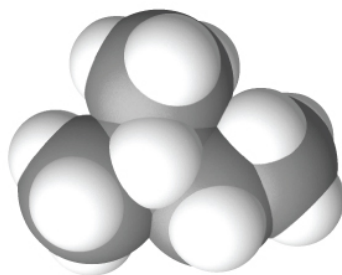
The shapes of molecules also affect the magnitudes of the dispersion forces between them. For example, boiling points for the isomers *n*-pentane,

isopentane, and neopentane (shown in [\[link\]](#)) are 36 °C, 27 °C, and 9.5 °C, respectively. Even though these compounds are composed of molecules with the same chemical formula, C_5H_{12} , the difference in boiling points suggests that dispersion forces in the liquid phase are different, being greatest for *n*-pentane and least for neopentane. The elongated shape of *n*-pentane provides a greater surface area available for contact between molecules, resulting in correspondingly stronger dispersion forces. The more compact shape of isopentane offers a smaller surface area available for intermolecular contact and, therefore, weaker dispersion forces. Neopentane molecules are the most compact of the three, offering the least available surface area for intermolecular contact and, hence, the weakest dispersion forces. This behavior is analogous to the connections that may be formed between strips of VELCRO brand fasteners: the greater the area of the strip's contact, the stronger the connection.

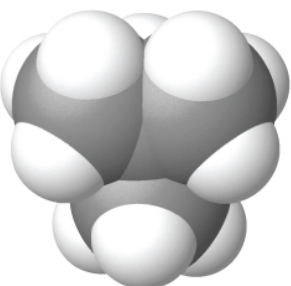
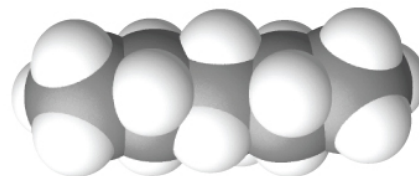
Small contact area,
weakest attraction



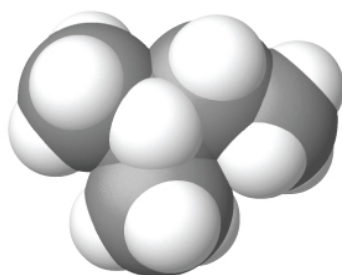
Less surface area,
less attraction



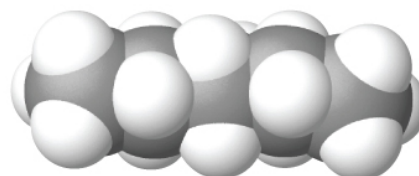
Large contact area,
strong attraction



neopentane
boiling point: 9.5 °C



isopentane
boiling point: 27 °C



n-pentane
boiling point: 36 °C

The strength of the dispersion forces increases with the contact area

between molecules, as demonstrated by the boiling points of these pentane isomers.

Note:

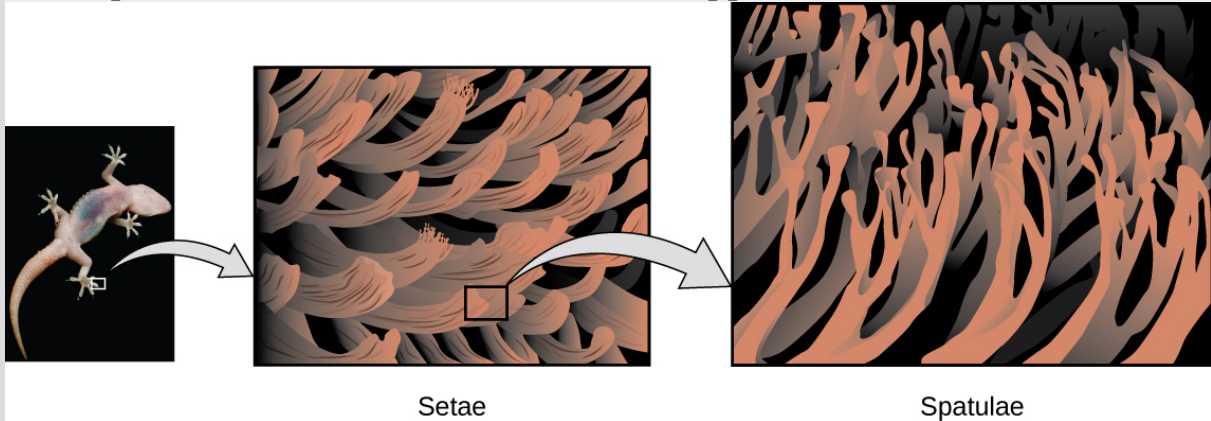
Geckos and Intermolecular Forces

Geckos have an amazing ability to adhere to most surfaces. They can quickly run up smooth walls and across ceilings that have no toe-holds, and they do this without having suction cups or a sticky substance on their toes. And while a gecko can lift its feet easily as it walks along a surface, if you attempt to pick it up, it sticks to the surface. How are geckos (as well as spiders and some other insects) able to do this? Although this phenomenon has been investigated for hundreds of years, scientists only recently uncovered the details of the process that allows geckos' feet to behave this way.

Geckos' toes are covered with hundreds of thousands of tiny hairs known as *setae*, with each seta, in turn, branching into hundreds of tiny, flat, triangular tips called *spatulae*. The huge numbers of spatulae on its setae provide a gecko, shown in [\[link\]](#), with a large total surface area for sticking to a surface. In 2000, Kellar Autumn, who leads a multi-institutional gecko research team, found that geckos adhered equally well to both polar silicon dioxide and nonpolar gallium arsenide. This proved that geckos stick to surfaces because of dispersion forces—weak intermolecular attractions arising from temporary, synchronized charge distributions between adjacent molecules. Although dispersion forces are very weak, the total attraction over millions of spatulae is large enough to support many times the gecko's weight.

In 2014, two scientists developed a model to explain how geckos can rapidly transition from “sticky” to “non-sticky.” Alex Greaney and Congcong Hu at Oregon State University described how geckos can achieve this by changing the angle between their spatulae and the surface. Geckos' feet, which are normally nonsticky, become sticky when a small shear force is applied. By curling and uncurling their toes, geckos can alternate between sticking and unsticking from a surface, and thus easily

move across it. Further investigations may eventually lead to the development of better adhesives and other applications.



Geckos' toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko's millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness "on" and "off." (credit photo: modification of work by "JC*+A!"/Flickr)

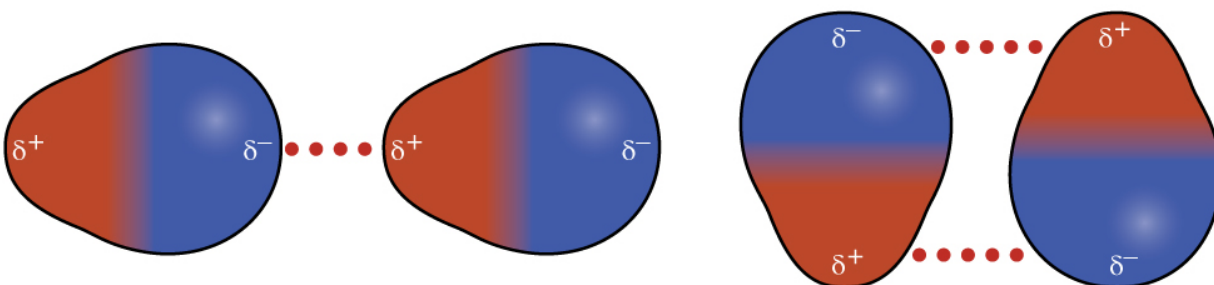
Note:



Watch this [video](#) to learn more about Kellar Autumn's research that determined that van der Waals forces are responsible for a gecko's ability to cling and climb.

Dipole-Dipole Attractions

Recall from the chapter on chemical bonding and molecular geometry that *polar* molecules have a partial positive charge on one side and a partial negative charge on the other side of the molecule—a separation of charge called a *dipole*. Consider a polar molecule such as hydrogen chloride, HCl. In the HCl molecule, the more electronegative Cl atom bears the partial negative charge, whereas the less electronegative H atom bears the partial positive charge. An attractive force between HCl molecules results from the attraction between the positive end of one HCl molecule and the negative end of another. This attractive force is called a **dipole-dipole attraction**—the electrostatic force between the partially positive end of one polar molecule and the partially negative end of another, as illustrated in [\[link\]](#).



This image shows two arrangements of polar molecules, such as HCl, that allow an attraction between the partial negative end of one molecule and the partial positive end of another.

The effect of a dipole-dipole attraction is apparent when we compare the properties of HCl molecules to nonpolar F_2 molecules. Both HCl and F_2 consist of the same number of atoms and have approximately the same molecular mass. At a temperature of 150 K, molecules of both substances would have the same average KE. However, the dipole-dipole attractions between HCl molecules are sufficient to cause them to “stick together” to form a liquid, whereas the relatively weaker dispersion forces between nonpolar F_2 molecules are not, and so this substance is gaseous at this

temperature. The higher normal boiling point of HCl (188 K) compared to F₂ (85 K) is a reflection of the greater strength of dipole-dipole attractions between HCl molecules, compared to the attractions between nonpolar F₂ molecules. We will often use values such as boiling or freezing points, or enthalpies of vaporization or fusion, as indicators of the relative strengths of IMFs of attraction present within different substances.

Example:**Dipole-Dipole Forces and Their Effects**

Predict which will have the higher boiling point: N₂ or CO. Explain your reasoning.

Solution

CO and N₂ are both diatomic molecules with masses of about 28 amu, so they experience similar London dispersion forces. Because CO is a polar molecule, it experiences dipole-dipole attractions. Because N₂ is nonpolar, its molecules cannot exhibit dipole-dipole attractions. The dipole-dipole attractions between CO molecules are comparably stronger than the dispersion forces between nonpolar N₂ molecules, so CO is expected to have the higher boiling point.

Check Your Learning

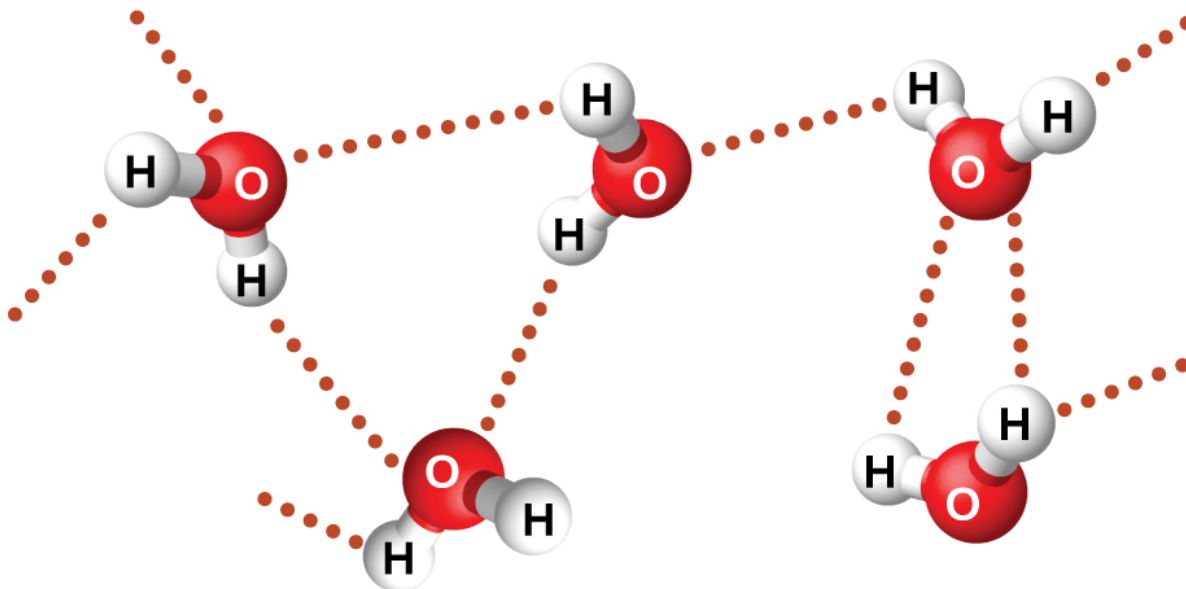
Predict which will have the higher boiling point: ICl or Br₂. Explain your reasoning.

Note:**Answer:**

ICl. ICl and Br₂ have similar masses (~160 amu) and therefore experience similar London dispersion forces. ICl is polar and thus also exhibits dipole-dipole attractions; Br₂ is nonpolar and does not. The relatively stronger dipole-dipole attractions require more energy to overcome, so ICl will have the higher boiling point.

Hydrogen Bonding

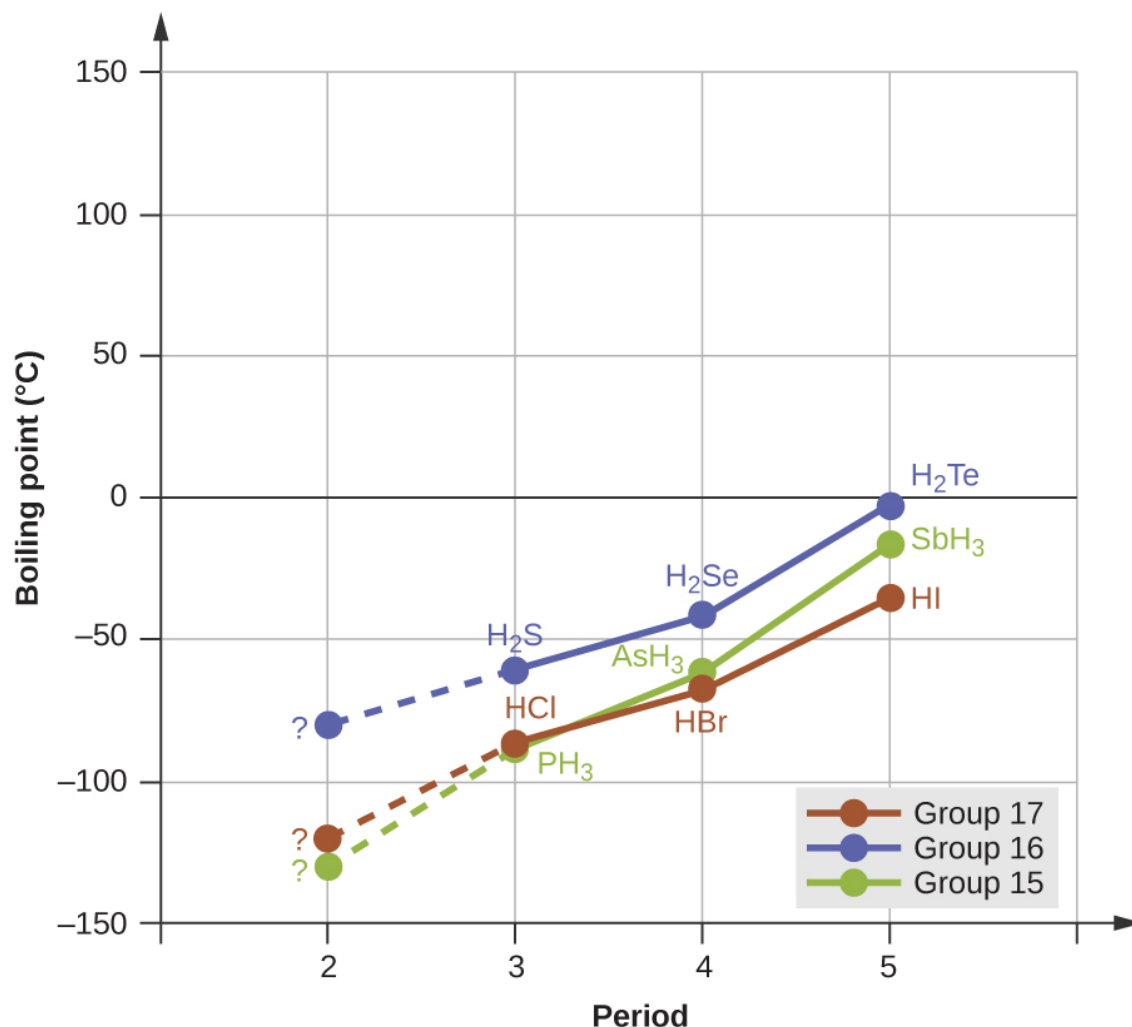
Nitrosyl fluoride (ONF, molecular mass 49 amu) is a gas at room temperature. Water (H₂O, molecular mass 18 amu) is a liquid, even though it has a lower molecular mass. We clearly cannot attribute this difference between the two compounds to dispersion forces. Both molecules have about the same shape and ONF is the heavier and larger molecule. It is, therefore, expected to experience more significant dispersion forces. Additionally, we cannot attribute this difference in boiling points to differences in the dipole moments of the molecules. Both molecules are polar and exhibit comparable dipole moments. The large difference between the boiling points is due to a particularly strong dipole-dipole attraction that may occur when a molecule contains a hydrogen atom bonded to a fluorine, oxygen, or nitrogen atom (the three most electronegative elements). The very large difference in electronegativity between the H atom (2.1) and the atom to which it is bonded (4.0 for an F atom, 3.5 for an O atom, or 3.0 for a N atom), combined with the very small size of a H atom and the relatively small sizes of F, O, or N atoms, leads to *highly concentrated partial charges* with these atoms. Molecules with F-H, O-H, or N-H moieties are very strongly attracted to similar moieties in nearby molecules, a particularly strong type of dipole-dipole attraction called **hydrogen bonding**. Examples of hydrogen bonds include HF···HF, H₂O···HOH, and H₃N···HNH₂, in which the hydrogen bonds are denoted by dots. [\[link\]](#) illustrates hydrogen bonding between water molecules.



Water molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

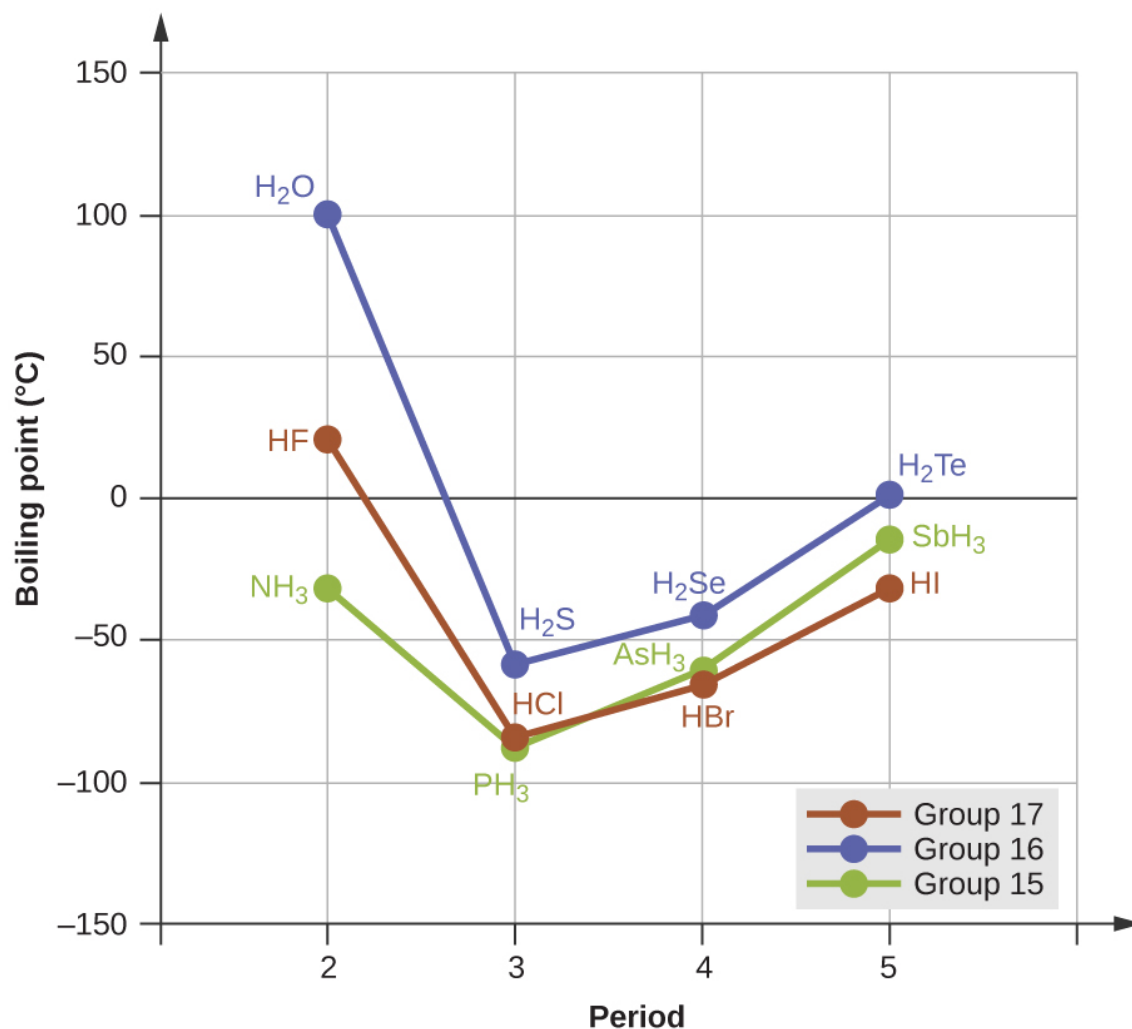
Despite use of the word “bond,” keep in mind that hydrogen bonds are *intermolecular* attractive forces, not *intramolecular* attractive forces (covalent bonds). Hydrogen bonds are much weaker than covalent bonds, only about 5 to 10% as strong, but are generally much stronger than other dipole-dipole attractions and dispersion forces.

Hydrogen bonds have a pronounced effect on the properties of condensed phases (liquids and solids). For example, consider the trends in boiling points for the binary hydrides of group 15 (NH₃, PH₃, AsH₃, and SbH₃), group 16 hydrides (H₂O, H₂S, H₂Se, and H₂Te), and group 17 hydrides (HF, HCl, HBr, and HI). The boiling points of the heaviest three hydrides for each group are plotted in [\[link\]](#). As we progress down any of these groups, the polarities of the molecules decrease slightly, whereas the sizes of the molecules increase substantially. The effect of increasingly stronger dispersion forces dominates that of increasingly weaker dipole-dipole attractions, and the boiling points are observed to increase steadily.



For the group 15, 16, and 17 hydrides, the boiling points for each class of compounds increase with increasing molecular mass for elements in periods 3, 4, and 5.

If we use this trend to predict the boiling points for the lightest hydride for each group, we would expect NH_3 to boil at about -120°C , H_2O to boil at about -80°C , and HF to boil at about -110°C . However, when we measure the boiling points for these compounds, we find that they are dramatically higher than the trends would predict, as shown in [\[link\]](#). The stark contrast between our naïve predictions and reality provides compelling evidence for the strength of hydrogen bonding.



In comparison to periods 3–5, the binary hydrides of period 2 elements in groups 17, 16 and 15 (F, O and N, respectively) exhibit anomalously high boiling points due to hydrogen bonding.

Example:

Effect of Hydrogen Bonding on Boiling Points

Consider the compounds dimethylether (CH_3OCH_3), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), and propane ($\text{CH}_3\text{CH}_2\text{CH}_3$). Their boiling points, not

necessarily in order, are $-42.1\text{ }^{\circ}\text{C}$, $-24.8\text{ }^{\circ}\text{C}$, and $78.4\text{ }^{\circ}\text{C}$. Match each compound with its boiling point. Explain your reasoning.

Solution

The VSEPR-predicted shapes of CH_3OCH_3 , $\text{CH}_3\text{CH}_2\text{OH}$, and $\text{CH}_3\text{CH}_2\text{CH}_3$ are similar, as are their molar masses (46 g/mol, 46 g/mol, and 44 g/mol, respectively), so they will exhibit similar dispersion forces. Since $\text{CH}_3\text{CH}_2\text{CH}_3$ is nonpolar, it may exhibit *only* dispersion forces. Because CH_3OCH_3 is polar, it will also experience dipole-dipole attractions. Finally, $\text{CH}_3\text{CH}_2\text{OH}$ has an $-\text{OH}$ group, and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of IMFs, and thus boiling points, is $\text{CH}_3\text{CH}_2\text{CH}_3 < \text{CH}_3\text{OCH}_3 < \text{CH}_3\text{CH}_2\text{OH}$. The boiling point of propane is $-42.1\text{ }^{\circ}\text{C}$, the boiling point of dimethylether is $-24.8\text{ }^{\circ}\text{C}$, and the boiling point of ethanol is $78.5\text{ }^{\circ}\text{C}$.

Check Your Learning

Ethane (CH_3CH_3) has a melting point of $-183\text{ }^{\circ}\text{C}$ and a boiling point of $-89\text{ }^{\circ}\text{C}$. Predict the melting and boiling points for methylamine (CH_3NH_2). Explain your reasoning.

Note:

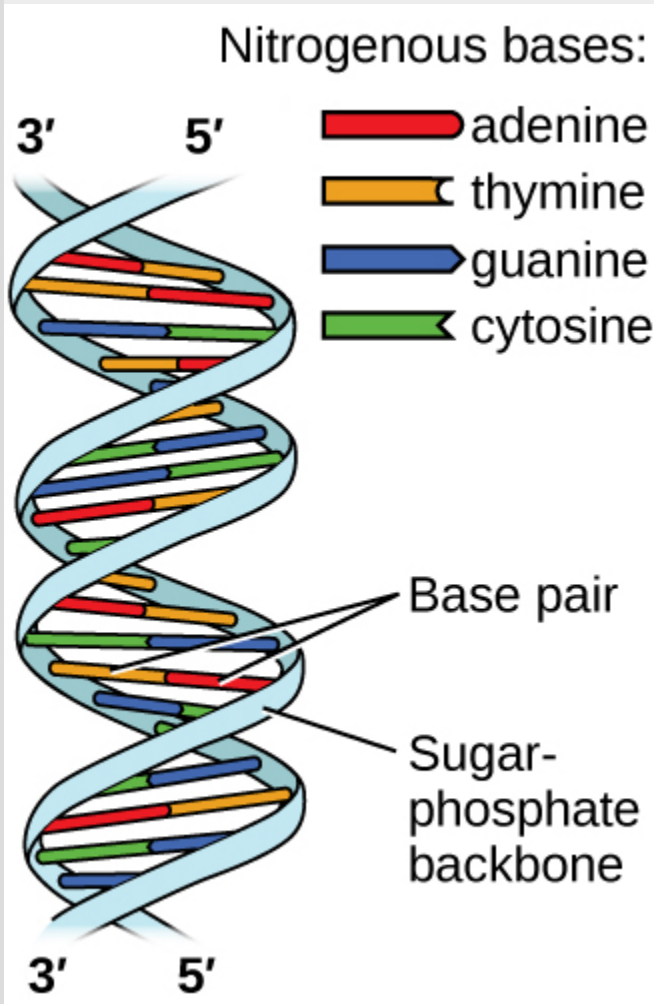
Answer:

The melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane. CH_3CH_3 and CH_3NH_2 are similar in size and mass, but methylamine possesses an $-\text{NH}$ group and therefore may exhibit hydrogen bonding. This greatly increases its IMFs, and therefore its melting and boiling points. It is difficult to predict values, but the known values are a melting point of $-93\text{ }^{\circ}\text{C}$ and a boiling point of $-6\text{ }^{\circ}\text{C}$.

Note:

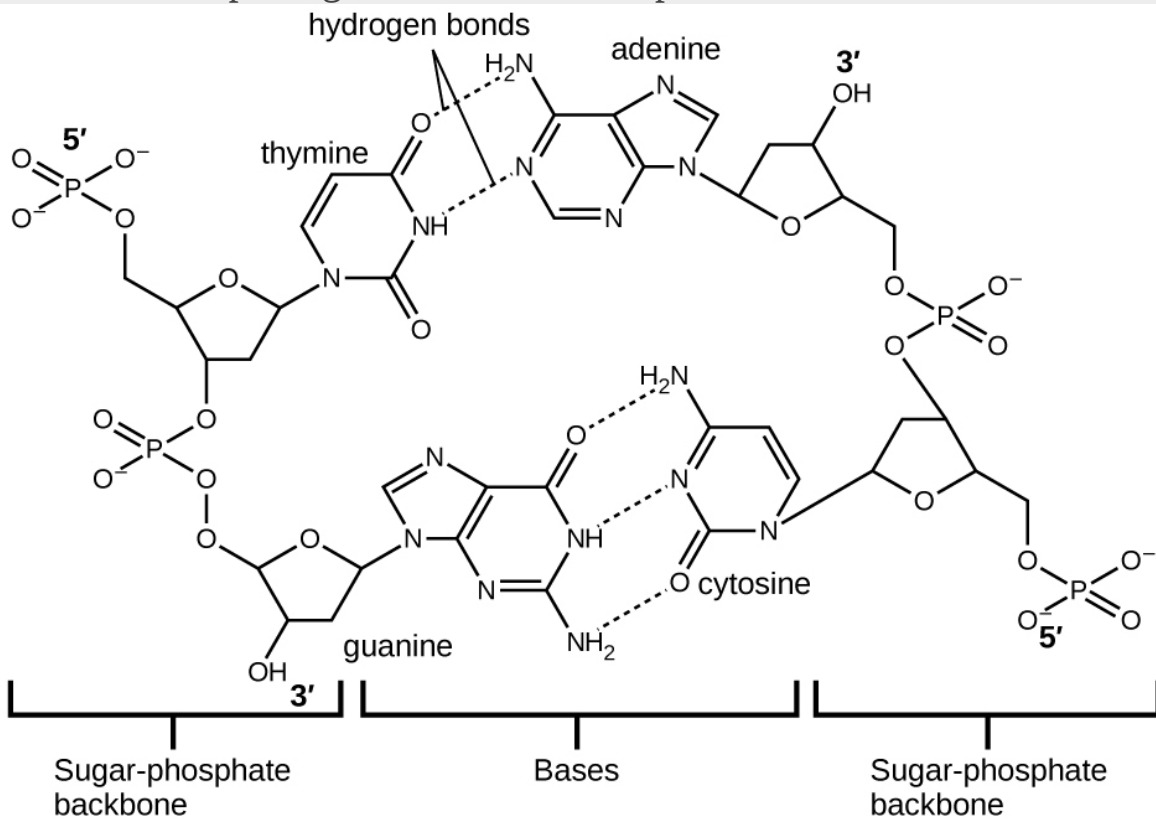
Hydrogen Bonding and DNA

Deoxyribonucleic acid (DNA) is found in every living organism and contains the genetic information that determines the organism's characteristics, provides the blueprint for making the proteins necessary for life, and serves as a template to pass this information on to the organism's offspring. A DNA molecule consists of two (anti-)parallel chains of repeating nucleotides, which form its well-known double helical structure, as shown in [\[link\]](#).



Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts)

Each nucleotide contains a (deoxyribose) sugar bound to a phosphate group on one side, and one of four nitrogenous bases on the other. Two of the bases, cytosine (C) and thymine (T), are single-ringed structures known as pyrimidines. The other two, adenine (A) and guanine (G), are double-ringed structures called purines. These bases form complementary base pairs consisting of one purine and one pyrimidine, with adenine pairing with thymine, and cytosine with guanine. Each base pair is held together by hydrogen bonding. A and T share two hydrogen bonds, C and G share three, and both pairings have a similar shape and structure [\[link\]](#).



The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called “complementary base pairs.”

The cumulative effect of millions of hydrogen bonds effectively holds the two strands of DNA together. Importantly, the two strands of DNA can relatively easily “unzip” down the middle since hydrogen bonds are

relatively weak compared to the covalent bonds that hold the atoms of the individual DNA molecules together. This allows both strands to function as a template for replication.

Key Concepts and Summary

The physical properties of condensed matter (liquids and solids) can be explained in terms of the kinetic molecular theory. In a liquid, intermolecular attractive forces hold the molecules in contact, although they still have sufficient KE to move past each other.

Intermolecular attractive forces, collectively referred to as van der Waals forces, are responsible for the behavior of liquids and solids and are electrostatic in nature. Dipole-dipole attractions result from the electrostatic attraction of the partial negative end of one dipolar molecule for the partial positive end of another. The temporary dipole that results from the motion of the electrons in an atom can induce a dipole in an adjacent atom and give rise to the London dispersion force. London forces increase with increasing molecular size. Hydrogen bonds are a special type of dipole-dipole attraction that results when hydrogen is bonded to one of the three most electronegative elements: F, O, or N.

Chemistry End of Chapter Exercises

Exercise:

Problem:

In terms of their bulk properties, how do liquids and solids differ?
How are they similar?

Solution:

Liquids and solids are similar in that they are matter composed of atoms, ions, or molecules. They are incompressible and have similar

densities that are both much larger than those of gases. They are different in that liquids have no fixed shape, and solids are rigid.

Exercise:

Problem:

In terms of the kinetic molecular theory, in what ways are liquids similar to solids? In what ways are liquids different from solids?

Exercise:

Problem:

In terms of the kinetic molecular theory, in what ways are liquids similar to gases? In what ways are liquids different from gases?

Solution:

They are similar in that the atoms or molecules are free to move from one position to another. They differ in that the particles of a liquid are confined to the shape of the vessel in which they are placed. In contrast, a gas will expand without limit to fill the space into which it is placed.

Exercise:

Problem:

Explain why liquids assume the shape of any container into which they are poured, whereas solids are rigid and retain their shape.

Exercise:

Problem:

What is the evidence that all neutral atoms and molecules exert attractive forces on each other?

Solution:

All atoms and molecules will condense into a liquid or solid in which the attractive forces exceed the kinetic energy of the molecules, at sufficiently low temperature.

Exercise:

Problem:

Open the [PhET States of Matter Simulation](#) to answer the following questions:

- (a) Select the Solid, Liquid, Gas tab. Explore by selecting different substances, heating and cooling the systems, and changing the state. What similarities do you notice between the four substances for each phase (solid, liquid, gas)? What differences do you notice?
- (b) For each substance, select each of the states and record the given temperatures. How do the given temperatures for each state correlate with the strengths of their intermolecular attractions? Explain.
- (c) Select the Interaction Potential tab, and use the default neon atoms. Move the Ne atom on the right and observe how the potential energy changes. Select the Total Force button, and move the Ne atom as before. When is the total force on each atom attractive and large enough to matter? Then select the Component Forces button, and move the Ne atom. When do the attractive (van der Waals) and repulsive (electron overlap) forces balance? How does this relate to the potential energy versus the distance between atoms graph? Explain.

Exercise:

Problem: Define the following and give an example of each:

- (a) dispersion force
- (b) dipole-dipole attraction
- (c) hydrogen bond

Solution:

(a) Dispersion forces occur as an atom develops a temporary dipole moment when its electrons are distributed asymmetrically about the nucleus. This structure is more prevalent in large atoms such as argon or radon. A second atom can then be distorted by the appearance of the dipole in the first atom. The electrons of the second atom are attracted toward the positive end of the first atom, which sets up a dipole in the second atom. The net result is rapidly fluctuating, temporary dipoles that attract one another (example: Ar). (b) A dipole-dipole attraction is a force that results from an electrostatic attraction of the positive end of one polar molecule for the negative end of another polar molecule (example: ICl molecules attract one another by dipole-dipole interaction). (c) Hydrogen bonds form whenever a hydrogen atom is bonded to one of the more electronegative atoms, such as a fluorine, oxygen, or nitrogen atom. The electrostatic attraction between the partially positive hydrogen atom in one molecule and the partially negative atom in another molecule gives rise to a strong dipole-dipole interaction called a hydrogen bond (example: $\text{HF} \cdots \text{HF}$).

Exercise:**Problem:**

The types of intermolecular forces in a substance are identical whether it is a solid, a liquid, or a gas. Why then does a substance change phase from a gas to a liquid or to a solid?

Exercise:**Problem:**

Why do the boiling points of the noble gases increase in the order $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe}$?

Solution:

The London forces typically increase as the number of electrons increase.

Exercise:**Problem:**

Neon and HF have approximately the same molecular masses.

- (a) Explain why the boiling points of Neon and HF differ.
- (b) Compare the change in the boiling points of Ne, Ar, Kr, and Xe with the change of the boiling points of HF, HCl, HBr, and HI, and explain the difference between the changes with increasing atomic or molecular mass.

Exercise:**Problem:**

Arrange each of the following sets of compounds in order of increasing boiling point temperature:

- (a) HCl, H₂O, SiH₄
- (b) F₂, Cl₂, Br₂
- (c) CH₄, C₂H₆, C₃H₈
- (d) O₂, NO, N₂

Solution:

(a) SiH₄ < HCl < H₂O; (b) F₂ < Cl₂ < Br₂; (c) CH₄ < C₂H₆ < C₃H₈; (d) N₂ < O₂ < NO

Exercise:**Problem:**

The molecular mass of butanol, C₄H₉OH, is 74.14; that of ethylene glycol, CH₂(OH)CH₂OH, is 62.08, yet their boiling points are 117.2 °C and 174 °C, respectively. Explain the reason for the difference.

Exercise:

Problem:

On the basis of intermolecular attractions, explain the differences in the boiling points of *n*-butane ($-1\text{ }^{\circ}\text{C}$) and chloroethane ($12\text{ }^{\circ}\text{C}$), which have similar molar masses.

Solution:

Only rather small dipole-dipole interactions from C-H bonds are available to hold *n*-butane in the liquid state. Chloroethane, however, has rather large dipole interactions because of the Cl-C bond; the interaction is therefore stronger, leading to a higher boiling point.

Exercise:**Problem:**

On the basis of dipole moments and/or hydrogen bonding, explain in a qualitative way the differences in the boiling points of acetone ($56.2\text{ }^{\circ}\text{C}$) and 1-propanol ($97.4\text{ }^{\circ}\text{C}$), which have similar molar masses.

Exercise:**Problem:**

The melting point of $\text{H}_2\text{O}(\text{s})$ is $0\text{ }^{\circ}\text{C}$. Would you expect the melting point of $\text{H}_2\text{S}(\text{s})$ to be $-85\text{ }^{\circ}\text{C}$, $0\text{ }^{\circ}\text{C}$, or $185\text{ }^{\circ}\text{C}$? Explain your answer.

Solution:

$-85\text{ }^{\circ}\text{C}$. Water has stronger hydrogen bonds so it melts at a higher temperature.

Exercise:**Problem:**

Silane (SiH_4), phosphine (PH_3), and hydrogen sulfide (H_2S) melt at $-185\text{ }^{\circ}\text{C}$, $-133\text{ }^{\circ}\text{C}$, and $-85\text{ }^{\circ}\text{C}$, respectively. What does this suggest about the polar character and intermolecular attractions of the three compounds?

Exercise:**Problem:**

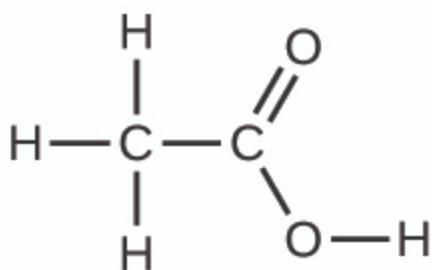
Explain why a hydrogen bond between two water molecules is weaker than a hydrogen bond between two hydrogen fluoride molecules.

Solution:

The hydrogen bond between two hydrogen fluoride molecules is stronger than that between two water molecules because the electronegativity of F is greater than that of O. Consequently, the partial negative charge on F is greater than that on O. The hydrogen bond between the partially positive H and the larger partially negative F will be stronger than that formed between H and O.

Exercise:**Problem:**

Under certain conditions, molecules of acetic acid, CH_3COOH , form “dimers,” pairs of acetic acid molecules held together by strong intermolecular attractions:

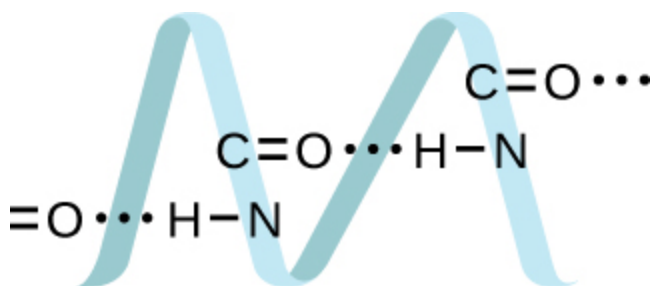


Draw a dimer of acetic acid, showing how two CH_3COOH molecules are held together, and stating the type of IMF that is responsible.

Exercise:

Problem:

Proteins are chains of amino acids that can form in a variety of arrangements, one of which is a helix. What kind of IMF is responsible for holding the protein strand in this shape? On the protein image, show the locations of the IMFs that hold the protein together:



Solution:

H-bonding is the principle IMF holding the protein strands together. The H-bonding is between the $\text{N}-\text{H}$ and $\text{C}=\text{O}$.

Exercise:**Problem:**

The density of liquid NH_3 is 0.64 g/mL; the density of gaseous NH_3 at STP is 0.0007 g/mL. Explain the difference between the densities of these two phases.

Exercise:**Problem:**

Identify the intermolecular forces present in the following solids:

- (a) $\text{CH}_3\text{CH}_2\text{OH}$
- (b) $\text{CH}_3\text{CH}_2\text{CH}_3$
- (c) $\text{CH}_3\text{CH}_2\text{Cl}$

Solution:

- (a) hydrogen bonding, dipole-dipole attraction, and dispersion forces;
- (b) dispersion forces; (c) dipole-dipole attraction and dispersion forces

Glossary

dipole-dipole attraction

intermolecular attraction between two permanent dipoles

dispersion force

(also, London dispersion force) attraction between two rapidly fluctuating, temporary dipoles; significant only when particles are very close together

hydrogen bonding

occurs when exceptionally strong dipoles attract; bonding that exists when hydrogen is bonded to one of the three most electronegative elements: F, O, or N

induced dipole

temporary dipole formed when the electrons of an atom or molecule are distorted by the instantaneous dipole of a neighboring atom or molecule

instantaneous dipole

temporary dipole that occurs for a brief moment in time when the electrons of an atom or molecule are distributed asymmetrically

intermolecular force

noncovalent attractive force between atoms, molecules, and/or ions

polarizability

measure of the ability of a charge to distort a molecule's charge distribution (electron cloud)

van der Waals force

attractive or repulsive force between molecules, including dipole-dipole, dipole-induced dipole, and London dispersion forces; does not include forces due to covalent or ionic bonding, or the attraction between ions and molecules

Phase Transitions

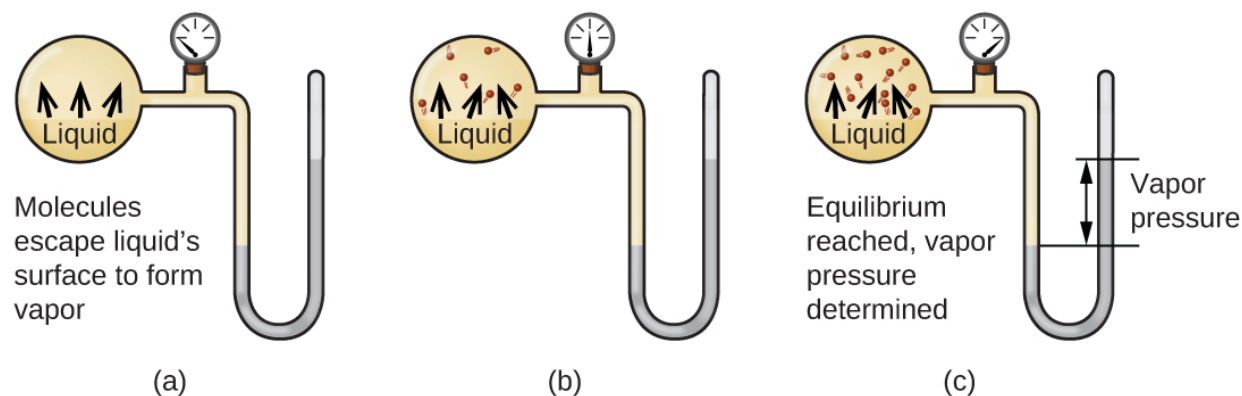
By the end of this section, you will be able to:

- Define phase transitions and phase transition temperatures
- Explain the relation between phase transition temperatures and intermolecular attractive forces
- Describe the processes represented by typical heating and cooling curves, and compute heat flows and enthalpy changes accompanying these processes

We witness and utilize changes of physical state, or phase transitions, in a great number of ways. As one example of global significance, consider the evaporation, condensation, freezing, and melting of water. These changes of state are essential aspects of our earth's water cycle as well as many other natural phenomena and technological processes of central importance to our lives. In this module, the essential aspects of phase transitions are explored.

Vaporization and Condensation

When a liquid vaporizes in a closed container, gas molecules cannot escape. As these gas phase molecules move randomly about, they will occasionally collide with the surface of the condensed phase, and in some cases, these collisions will result in the molecules re-entering the condensed phase. The change from the gas phase to the liquid is called **condensation**. When the rate of condensation becomes equal to the rate of **vaporization**, neither the amount of the liquid nor the amount of the vapor in the container changes. The vapor in the container is then said to be *in equilibrium* with the liquid. Keep in mind that this is not a static situation, as molecules are continually exchanged between the condensed and gaseous phases. Such is an example of a **dynamic equilibrium**, the status of a system in which reciprocal processes (for example, vaporization and condensation) occur at equal rates. The pressure exerted by the vapor in equilibrium with a liquid in a closed container at a given temperature is called the liquid's **vapor pressure** (or equilibrium vapor pressure). The area of the surface of the liquid in contact with a vapor and the size of the vessel have no effect on the vapor pressure, although they do affect the time required for the equilibrium to be reached. We can measure the vapor pressure of a liquid by placing a sample in a closed container, like that illustrated in [\[link\]](#), and using a manometer to measure the increase in pressure that is due to the vapor in equilibrium with the condensed phase.



In a closed container, dynamic equilibrium is reached when (a) the rate of molecules escaping from the liquid to become the gas (b) increases and eventually (c) equals the rate of gas molecules entering the liquid. When this equilibrium is reached, the vapor pressure of the gas is constant, although the vaporization and condensation processes continue.

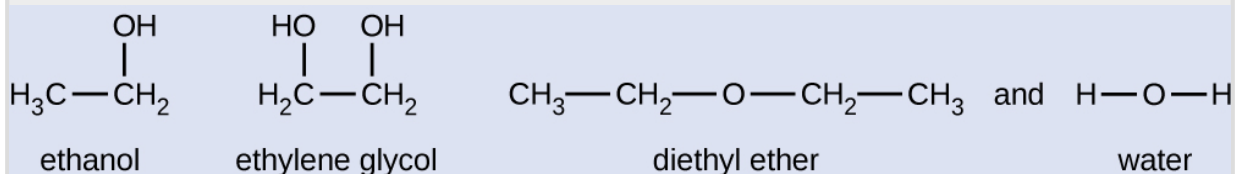
The chemical identities of the molecules in a liquid determine the types (and strengths) of intermolecular attractions possible; consequently, different substances will exhibit different equilibrium vapor pressures. Relatively strong intermolecular attractive forces will serve to impede vaporization as well as favoring "recapture"

of gas-phase molecules when they collide with the liquid surface, resulting in a relatively low vapor pressure. Weak intermolecular attractions present less of a barrier to vaporization, and a reduced likelihood of gas recapture, yielding relatively high vapor pressures. The following example illustrates this dependence of vapor pressure on intermolecular attractive forces.

Example:

Explaining Vapor Pressure in Terms of IMFs

Given the shown structural formulas for these four compounds, explain their relative vapor pressures in terms of types and extents of IMFs:



Solution

Diethyl ether has a very small dipole and most of its intermolecular attractions are London forces. Although this molecule is the largest of the four under consideration, its IMFs are the weakest and, as a result, its molecules most readily escape from the liquid. It also has the highest vapor pressure. Due to its smaller size, ethanol exhibits weaker dispersion forces than diethyl ether. However, ethanol is capable of hydrogen bonding and, therefore, exhibits stronger overall IMFs, which means that fewer molecules escape from the liquid at any given temperature, and so ethanol has a lower vapor pressure than diethyl ether. Water is much smaller than either of the previous substances and exhibits weaker dispersion forces, but its extensive hydrogen bonding provides stronger intermolecular attractions, fewer molecules escaping the liquid, and a lower vapor pressure than for either diethyl ether or ethanol. Ethylene glycol has two –OH groups, so, like water, it exhibits extensive hydrogen bonding. It is much larger than water and thus experiences larger London forces. Its overall IMFs are the largest of these four substances, which means its vaporization rate will be the slowest and, consequently, its vapor pressure the lowest.

Check Your Learning

At 20 °C, the vapor pressures of several alcohols are given in this table. Explain these vapor pressures in terms of types and extents of IMFs for these alcohols:

Compound	methanol CH ₃ OH	ethanol C ₂ H ₅ OH	propanol C ₃ H ₇ OH	butanol C ₄ H ₉ OH
Vapor Pressure at 20 °C	11.9 kPa	5.95 kPa	2.67 kPa	0.56 kPa

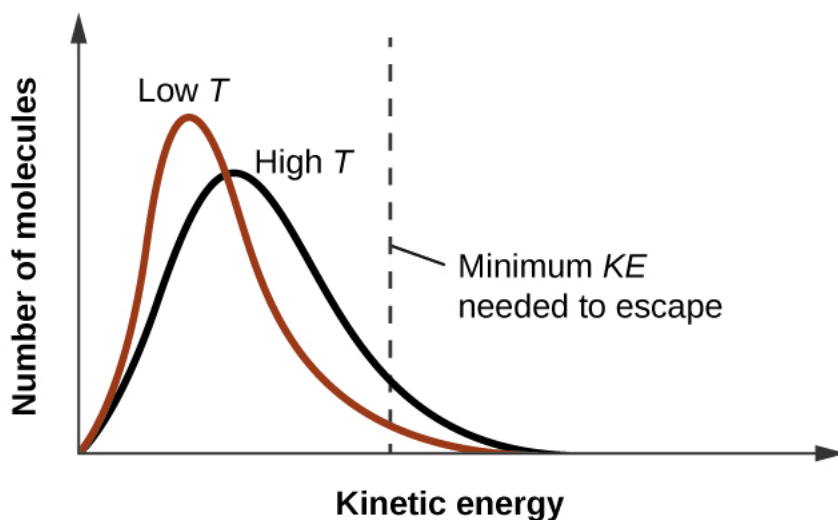
Note:

Answer:

All these compounds exhibit hydrogen bonding; these strong IMFs are difficult for the molecules to overcome, so the vapor pressures are relatively low. As the size of molecule increases from methanol to butanol, dispersion forces increase, which means that the vapor pressures decrease as observed:

$$P_{\text{methanol}} > P_{\text{ethanol}} > P_{\text{propanol}} > P_{\text{butanol}}$$

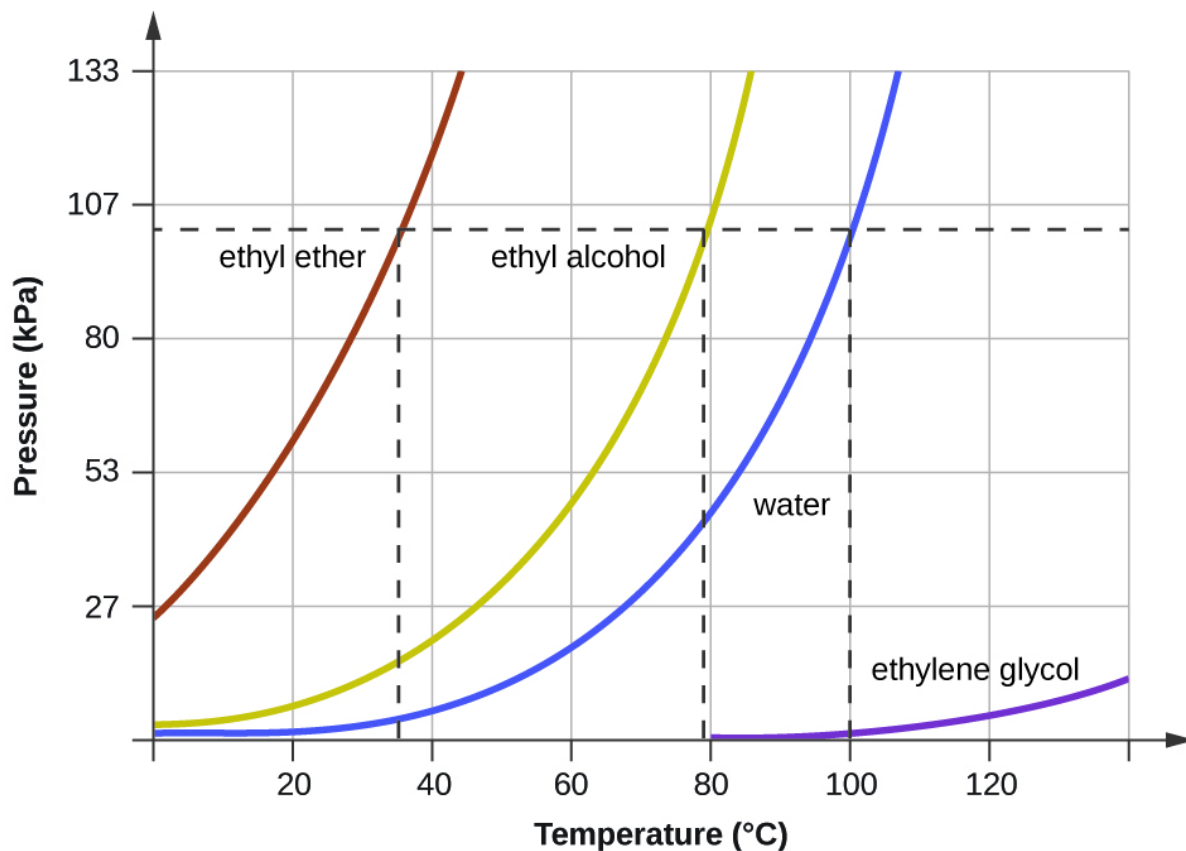
As temperature increases, the vapor pressure of a liquid also increases due to the increased average KE of its molecules. Recall that at any given temperature, the molecules of a substance experience a range of kinetic energies, with a certain fraction of molecules having a sufficient energy to overcome IMF and escape the liquid (vaporize). At a higher temperature, a greater fraction of molecules have enough energy to escape from the liquid, as shown in [\[link\]](#). The escape of more molecules per unit of time and the greater average speed of the molecules that escape both contribute to the higher vapor pressure.



Temperature affects the distribution of kinetic energies for the molecules in a liquid. At the higher temperature, more molecules have the necessary kinetic energy, KE, to escape from the liquid into the gas phase.

Boiling Points

When the vapor pressure increases enough to equal the external atmospheric pressure, the liquid reaches its boiling point. The **boiling point** of a liquid is the temperature at which its equilibrium vapor pressure is equal to the pressure exerted on the liquid by its gaseous surroundings. For liquids in open containers, this pressure is that due to the earth's atmosphere. The **normal boiling point** of a liquid is defined as its boiling point when surrounding pressure is equal to 1 atm (101.3 kPa). [\[link\]](#) shows the variation in vapor pressure with temperature for several different substances. Considering the definition of boiling point, these curves may be seen as depicting the dependence of a liquid's boiling point on surrounding pressure.



The boiling points of liquids are the temperatures at which their equilibrium vapor pressures equal the pressure of the surrounding atmosphere. Normal boiling points are those corresponding to a pressure of 1 atm (101.3 kPa.)

Example:

A Boiling Point at Reduced Pressure

A typical atmospheric pressure in Leadville, Colorado (elevation 10,200 feet) is 68 kPa. Use the graph in [\[link\]](#) to determine the boiling point of water at this elevation.

Solution

The graph of the vapor pressure of water versus temperature in [\[link\]](#) indicates that the vapor pressure of water is 68 kPa at about 90 °C. Thus, at about 90 °C, the vapor pressure of water will equal the atmospheric pressure in Leadville, and water will boil.

Check Your Learning

The boiling point of ethyl ether was measured to be 10 °C at a base camp on the slopes of Mount Everest. Use [\[link\]](#) to determine the approximate atmospheric pressure at the camp.

Note:

Answer:

Approximately 40 kPa (0.4 atm)

The quantitative relation between a substance's vapor pressure and its temperature is described by the **Clausius-Clapeyron equation**:

Equation:

$$P = Ae^{-\Delta H_{\text{vap}}/RT}$$

where ΔH_{vap} is the enthalpy of vaporization for the liquid, R is the gas constant, and A is a constant whose value depends on the chemical identity of the substance. Temperature T must be in Kelvin in this equation. This equation is often rearranged into logarithmic form to yield the linear equation:

Equation:

$$\ln P = -\frac{\Delta H_{\text{vap}}}{RT} + \ln A$$

This linear equation may be expressed in a two-point format that is convenient for use in various computations, as demonstrated in the example exercises that follow. If at temperature T_1 , the vapor pressure is P_1 , and at temperature T_2 , the vapor pressure is P_2 , the corresponding linear equations are:

Equation:

$$\ln P_1 = -\frac{\Delta H_{\text{vap}}}{RT_1} + \ln A \quad \text{and} \quad \ln P_2 = -\frac{\Delta H_{\text{vap}}}{RT_2} + \ln A$$

Since the constant, A , is the same, these two equations may be rearranged to isolate $\ln A$ and then set them equal to one another:

Equation:

$$\ln P_1 + \frac{\Delta H_{\text{vap}}}{RT_1} = \ln P_2 + \frac{\Delta H_{\text{vap}}}{RT_2}$$

which can be combined into:

Equation:

$$\ln \left(\frac{P_2}{P_1} \right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Example:

Estimating Enthalpy of Vaporization

Isooctane (2,2,4-trimethylpentane) has an octane rating of 100. It is used as one of the standards for the octane-rating system for gasoline. At 34.0 °C, the vapor pressure of isooctane is 10.0 kPa, and at 98.8 °C, its vapor pressure is 100.0 kPa. Use this information to estimate the enthalpy of vaporization for isooctane.

Solution

The enthalpy of vaporization, ΔH_{vap} , can be determined by using the Clausius-Clapeyron equation:

Equation:

$$\ln \left(\frac{P_2}{P_1} \right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Since we have two vapor pressure-temperature values ($T_1 = 34.0\text{ }^\circ\text{C} = 307.2\text{ K}$, $P_1 = 10.0\text{ kPa}$ and $T_2 = 98.8\text{ }^\circ\text{C} = 372.0\text{ K}$, $P_2 = 100\text{ kPa}$), we can substitute them into this equation and solve for ΔH_{vap} . Rearranging the Clausius-Clapeyron equation and solving for ΔH_{vap} yields:

Equation:

$$\Delta H_{\text{vap}} = \frac{R \cdot \ln \left(\frac{P_2}{P_1} \right)}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} = \frac{(8.3145\text{ J/mol}\cdot\text{K}) \cdot \ln \left(\frac{100\text{ kPa}}{10.0\text{ kPa}} \right)}{\left(\frac{1}{307.2\text{ K}} - \frac{1}{372.0\text{ K}} \right)} = 33,800\text{ J/mol} = 33.8\text{ kJ/mol}$$

Note that the pressure can be in any units, so long as they agree for both P values, but the temperature must be in kelvin for the Clausius-Clapeyron equation to be valid.

Check Your Learning

At $20.0\text{ }^\circ\text{C}$, the vapor pressure of ethanol is 5.95 kPa , and at $63.5\text{ }^\circ\text{C}$, its vapor pressure is 53.3 kPa . Use this information to estimate the enthalpy of vaporization for ethanol.

Note:

Answer:

$41,360\text{ J/mol}$ or 41.4 kJ/mol

Example:

Estimating Temperature (or Vapor Pressure)

For benzene (C_6H_6), the normal boiling point is $80.1\text{ }^\circ\text{C}$ and the enthalpy of vaporization is 30.8 kJ/mol . What is the boiling point of benzene in Denver, where atmospheric pressure = 83.4 kPa ?

Solution

If the temperature and vapor pressure are known at one point, along with the enthalpy of vaporization, ΔH_{vap} , then the temperature that corresponds to a different vapor pressure (or the vapor pressure that corresponds to a different temperature) can be determined by using the Clausius-Clapeyron equation:

Equation:

$$\ln \left(\frac{P_2}{P_1} \right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Since the normal boiling point is the temperature at which the vapor pressure equals atmospheric pressure at sea level, we know one vapor pressure-temperature value ($T_1 = 80.1\text{ }^\circ\text{C} = 353.3\text{ K}$, $P_1 = 101.3\text{ kPa}$, $\Delta H_{\text{vap}} = 30.8\text{ kJ/mol}$) and want to find the temperature (T_2) that corresponds to vapor pressure $P_2 = 83.4\text{ kPa}$. We can substitute these values into the Clausius-Clapeyron equation and then solve for T_2 . Rearranging the Clausius-Clapeyron equation and solving for T_2 yields:

Equation:

$$T_2 = \left(\frac{-R \cdot \ln \left(\frac{P_2}{P_1} \right)}{\Delta H_{\text{vap}}} + \frac{1}{T_1} \right)^{-1} = \left(\frac{-(8.3145\text{ J/mol}\cdot\text{K}) \cdot \ln \left(\frac{83.4\text{ kPa}}{101.3\text{ kPa}} \right)}{30,800\text{ J/mol}} + \frac{1}{353.3\text{ K}} \right)^{-1} = 346.9\text{ K or }73.8\text{ }^\circ\text{C}$$

Check Your Learning

For acetone ($\text{CH}_3)_2\text{CO}$, the normal boiling point is $56.5\text{ }^\circ\text{C}$ and the enthalpy of vaporization is 31.3 kJ/mol . What is the vapor pressure of acetone at $25.0\text{ }^\circ\text{C}$?

Note:

Answer:

30.1 kPa

Enthalpy of Vaporization

Vaporization is an endothermic process. The cooling effect can be evident when you leave a swimming pool or a shower. When the water on your skin evaporates, it removes heat from your skin and causes you to feel cold. The energy change associated with the vaporization process is the enthalpy of vaporization, ΔH_{vap} . For example, the vaporization of water at standard temperature is represented by:

Equation:



As described in the chapter on thermochemistry, the reverse of an endothermic process is exothermic. And so, the condensation of a gas releases heat:

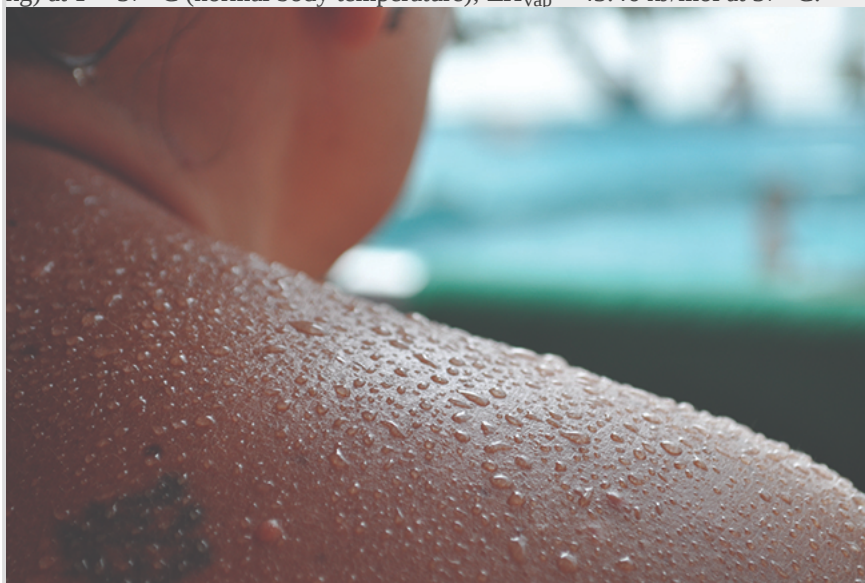
Equation:



Example:

Using Enthalpy of Vaporization

One way our body is cooled is by evaporation of the water in sweat ([link](#)). In very hot climates, we can lose as much as 1.5 L of sweat per day. Although sweat is not pure water, we can get an approximate value of the amount of heat removed by evaporation by assuming that it is. How much heat is required to evaporate 1.5 L of water (1.5 kg) at $T = 37^\circ\text{C}$ (normal body temperature); $\Delta H_{\text{vap}} = 43.46 \text{ kJ/mol}$ at 37°C .



Evaporation of sweat helps cool the body. (credit: "Kullez"/Flickr)

Solution

We start with the known volume of sweat (approximated as just water) and use the given information to convert to the amount of heat needed:

Equation:

$$1.5 \cancel{\text{ L}} \times \frac{1000 \cancel{\text{ g}}}{1 \cancel{\text{ L}}} \times \frac{1 \cancel{\text{ mol}}}{18 \cancel{\text{ g}}} \times \frac{43.46 \text{ kJ}}{1 \cancel{\text{ mol}}} = 3.6 \times 10^3 \text{ kJ}$$

Thus, 3600 kJ of heat are removed by the evaporation of 1.5 L of water.

Check Your Learning

How much heat is required to evaporate 100.0 g of liquid ammonia, NH_3 , at its boiling point if its enthalpy of vaporization is 4.8 kJ/mol?

Note:**Answer:**

28 kJ

Melting and Freezing

When we heat a crystalline solid, we increase the average energy of its atoms, molecules, or ions and the solid gets hotter. At some point, the added energy becomes large enough to partially overcome the forces holding the molecules or ions of the solid in their fixed positions, and the solid begins the process of transitioning to the liquid state, or **melting**. At this point, the temperature of the solid stops rising, despite the continual input of heat, and it remains constant until all of the solid is melted. Only after all of the solid has melted will continued heating increase the temperature of the liquid ([link](#)).



(a)



(b)



(c)



(d)

(a) This beaker of ice has a temperature of $-12.0\text{ }^{\circ}\text{C}$. (b) After 10 minutes the ice has absorbed enough heat from the air to warm to $0\text{ }^{\circ}\text{C}$. A small amount has melted. (c) Thirty minutes later, the ice has absorbed more heat, but its temperature is still $0\text{ }^{\circ}\text{C}$. The ice melts without changing its temperature. (d) Only after all the ice has melted does the heat absorbed cause the temperature to increase to $22.2\text{ }^{\circ}\text{C}$. (credit: modification of work by Mark Ott)

If we stop heating during melting and place the mixture of solid and liquid in a perfectly insulated container so no heat can enter or escape, the solid and liquid phases remain in equilibrium. This is almost the situation with a mixture of ice and water in a very good thermos bottle; almost no heat gets in or out, and the mixture of solid ice and liquid water remains for hours. In a mixture of solid and liquid at equilibrium, the reciprocal processes of

melting and **freezing** occur at equal rates, and the quantities of solid and liquid therefore remain constant. The temperature at which the solid and liquid phases of a given substance are in equilibrium is called the **melting point** of the solid or the **freezing point** of the liquid. Use of one term or the other is normally dictated by the direction of the phase transition being considered, for example, solid to liquid (melting) or liquid to solid (freezing).

The enthalpy of fusion and the melting point of a crystalline solid depend on the strength of the attractive forces between the units present in the crystal. Molecules with weak attractive forces form crystals with low melting points. Crystals consisting of particles with stronger attractive forces melt at higher temperatures.

The amount of heat required to change one mole of a substance from the solid state to the liquid state is the enthalpy of fusion, ΔH_{fus} of the substance. The enthalpy of fusion of ice is 6.0 kJ/mol at 0 °C. Fusion (melting) is an endothermic process:

Equation:



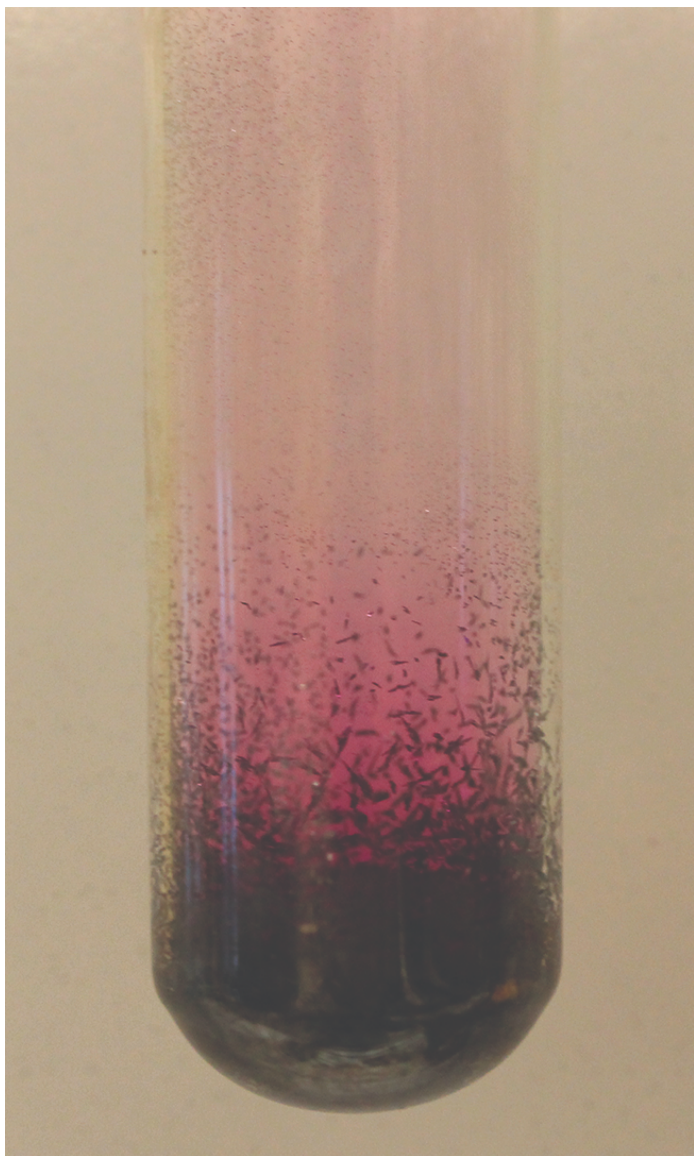
The reciprocal process, freezing, is an exothermic process whose enthalpy change is -6.0 kJ/mol at 0 °C:

Equation:



Sublimation and Deposition

Some solids can transition directly into the gaseous state, bypassing the liquid state, via a process known as **sublimation**. At room temperature and standard pressure, a piece of dry ice (solid CO_2) sublimates, appearing to gradually disappear without ever forming any liquid. Snow and ice sublime at temperatures below the melting point of water, a slow process that may be accelerated by winds and the reduced atmospheric pressures at high altitudes. When solid iodine is warmed, the solid sublimates and a vivid purple vapor forms ([link](#)). The reverse of sublimation is called **deposition**, a process in which gaseous substances condense directly into the solid state, bypassing the liquid state. The formation of frost is an example of deposition.



Sublimation of solid iodine in the bottom of the tube produces a purple gas that subsequently deposits as solid iodine on the colder part of the tube above. (credit: modification of work by Mark Ott)

Like vaporization, the process of sublimation requires an input of energy to overcome intermolecular attractions. The enthalpy of sublimation, ΔH_{sub} , is the energy required to convert one mole of a substance from the solid to the gaseous state. For example, the sublimation of carbon dioxide is represented by:

Equation:



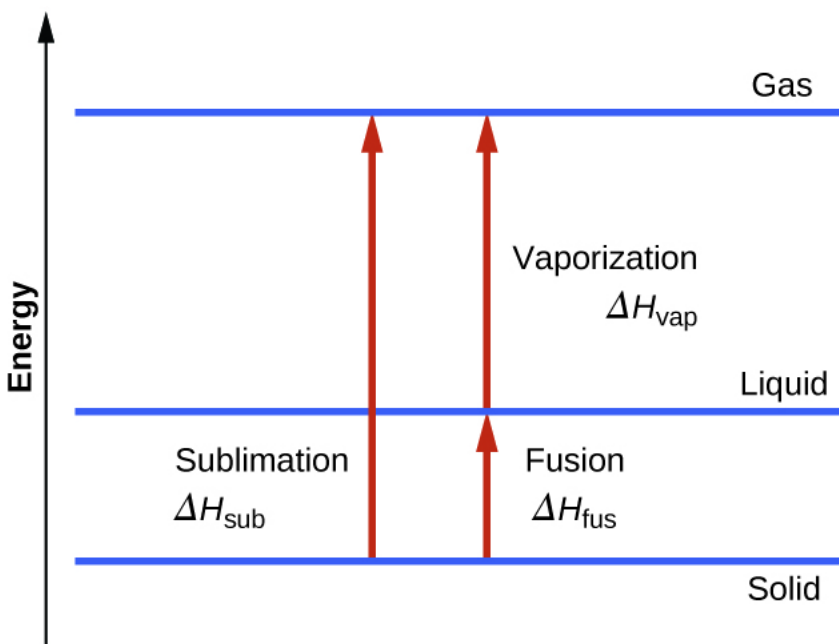
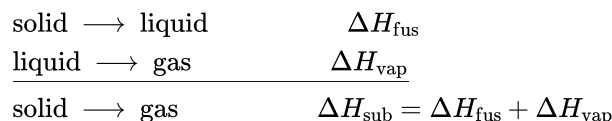
Likewise, the enthalpy change for the reverse process of deposition is equal in magnitude but opposite in sign to that for sublimation:

Equation:



Consider the extent to which intermolecular attractions must be overcome to achieve a given phase transition. Converting a solid into a liquid requires that these attractions be only partially overcome; transition to the gaseous state requires that they be completely overcome. As a result, the enthalpy of fusion for a substance is less than its enthalpy of vaporization. This same logic can be used to derive an approximate relation between the enthalpies of all phase changes for a given substance. Though not an entirely accurate description, sublimation may be conveniently modeled as a sequential two-step process of melting followed by vaporization in order to apply Hess's Law. Viewed in this manner, the enthalpy of sublimation for a substance may be estimated as the sum of its enthalpies of fusion and vaporization, as illustrated in [\[link\]](#). For example:

Equation:



For a given substance, the sum of its enthalpy of fusion and enthalpy of vaporization is approximately equal to its enthalpy of sublimation.

Heating and Cooling Curves

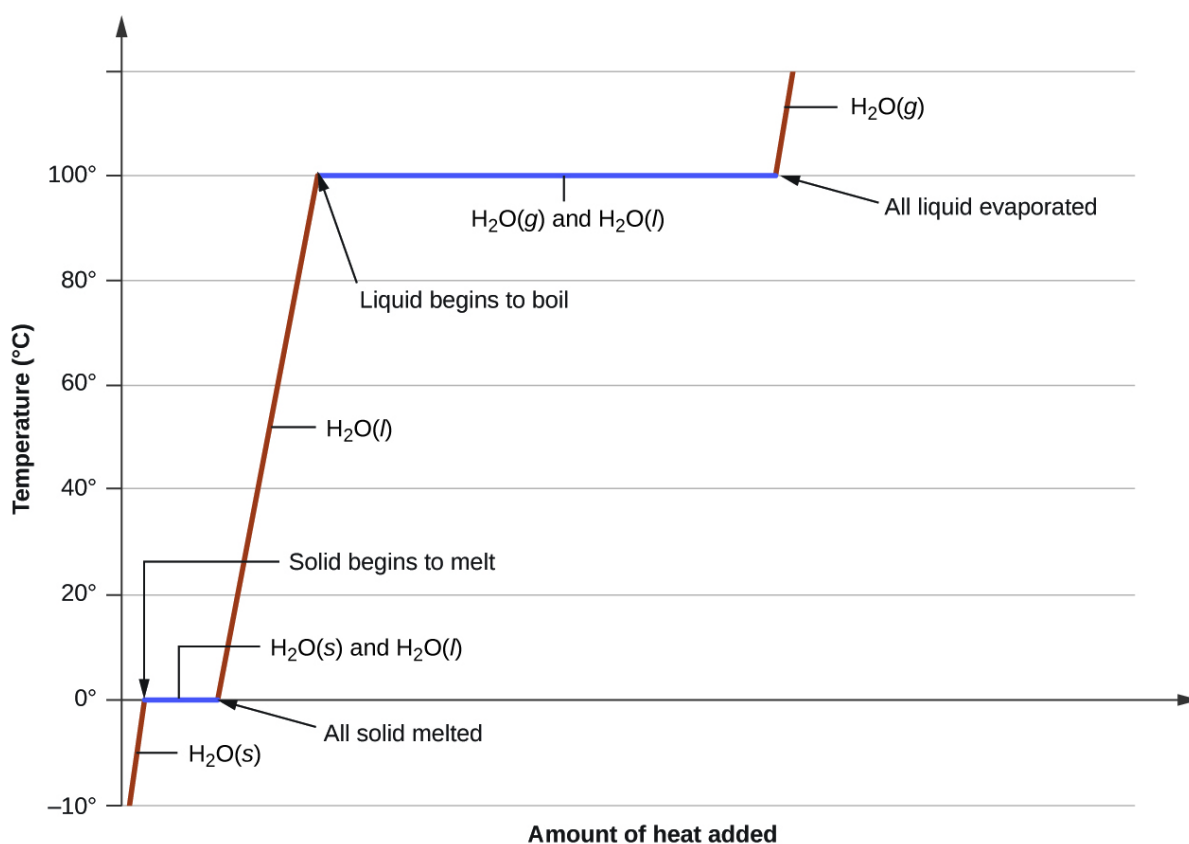
In the chapter on thermochemistry, the relation between the amount of heat absorbed or released by a substance, q , and its accompanying temperature change, ΔT , was introduced:

Equation:

$$q = mc\Delta T$$

where m is the mass of the substance and c is its specific heat. The relation applies to matter being heated or cooled, but not undergoing a change in state. When a substance being heated or cooled reaches a temperature corresponding to one of its phase transitions, further gain or loss of heat is a result of diminishing or enhancing intermolecular attractions, instead of increasing or decreasing molecular kinetic energies. While a substance is undergoing a change in state, its temperature remains constant. [\[link\]](#) shows a typical heating curve.

Consider the example of heating a pot of water to boiling. A stove burner will supply heat at a roughly constant rate; initially, this heat serves to increase the water's temperature. When the water reaches its boiling point, the temperature remains constant despite the continued input of heat from the stove burner. This same temperature is maintained by the water as long as it is boiling. If the burner setting is increased to provide heat at a greater rate, the water temperature does not rise, but instead the boiling becomes more vigorous (rapid). This behavior is observed for other phase transitions as well: For example, temperature remains constant while the change of state is in progress.



A typical heating curve for a substance depicts changes in temperature that result as the substance absorbs increasing amounts of heat. Plateaus in the curve (regions of constant temperature) are exhibited when the substance undergoes phase transitions.

Example:**Total Heat Needed to Change Temperature and Phase for a Substance**

How much heat is required to convert 135 g of ice at -15°C into water vapor at 120°C ?

Solution

The transition described involves the following steps:

1. Heat ice from $-15\text{ }^{\circ}\text{C}$ to $0\text{ }^{\circ}\text{C}$
2. Melt ice
3. Heat water from $0\text{ }^{\circ}\text{C}$ to $100\text{ }^{\circ}\text{C}$
4. Boil water
5. Heat steam from $100\text{ }^{\circ}\text{C}$ to $120\text{ }^{\circ}\text{C}$

The heat needed to change the temperature of a given substance (with no change in phase) is: $q = m \times c \times \Delta T$ (see previous chapter on thermochemistry). The heat needed to induce a given change in phase is given by $q = n \times \Delta H$.

Using these equations with the appropriate values for specific heat of ice, water, and steam, and enthalpies of fusion and vaporization, we have:

Equation:

$$q_{\text{total}} = (m \cdot c \cdot \Delta T)_{\text{ice}} + n \cdot \Delta H_{\text{fus}} + (m \cdot c \cdot \Delta T)_{\text{water}} + n \cdot \Delta H_{\text{vap}} + (m \cdot c \cdot \Delta T)_{\text{steam}}$$

Equation:

$$\begin{aligned} &= (135\text{ g} \cdot 2.09\text{ J/g} \cdot ^{\circ}\text{C} \cdot 15^{\circ}\text{C}) + \left(135 \cdot \frac{1\text{ mol}}{18.02\text{ g}} \cdot 6.01\text{ kJ/mol}\right) \\ &+ (135\text{ g} \cdot 4.18\text{ J/g} \cdot ^{\circ}\text{C} \cdot 100^{\circ}\text{C}) + \left(135\text{ g} \cdot \frac{1\text{ mol}}{18.02\text{ g}} \cdot 40.67\text{ kJ/mol}\right) \\ &+ (135\text{ g} \cdot 1.84\text{ J/g} \cdot ^{\circ}\text{C} \cdot 20^{\circ}\text{C}) \\ &= 4230\text{ J} + 45.0\text{ kJ} + 56,500\text{ J} + 305\text{ kJ} + 4970\text{ J} \end{aligned}$$

Converting the quantities in J to kJ permits them to be summed, yielding the total heat required:

Equation:

$$= 4.23\text{ kJ} + 45.0\text{ kJ} + 56.5\text{ kJ} + 305\text{ kJ} + 4.97\text{ kJ} = 416\text{ kJ}$$

Check Your Learning

What is the total amount of heat released when 94.0 g water at $80.0\text{ }^{\circ}\text{C}$ cools to form ice at $-30.0\text{ }^{\circ}\text{C}$?

Note:

Answer:

68.7 kJ

Key Concepts and Summary

Phase transitions are processes that convert matter from one physical state into another. There are six phase transitions between the three phases of matter. Melting, vaporization, and sublimation are all endothermic processes, requiring an input of heat to overcome intermolecular attractions. The reciprocal transitions of freezing, condensation, and deposition are all exothermic processes, involving heat as intermolecular attractive forces are established or strengthened. The temperatures at which phase transitions occur are determined by the relative strengths of intermolecular attractions and are, therefore, dependent on the chemical identity of the substance.

Key Equations

- $P = Ae^{-\Delta H_{\text{vap}}/RT}$

- $\ln P = -\frac{\Delta H_{\text{vap}}}{RT} + \ln A$
- $\ln \left(\frac{P_2}{P_1} \right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$

Chemistry End of Chapter Exercises

Exercise:

Problem:

Heat is added to boiling water. Explain why the temperature of the boiling water does not change. What does change?

Exercise:

Problem:

Heat is added to ice at 0 °C. Explain why the temperature of the ice does not change. What does change?

Solution:

The heat is absorbed by the ice, providing the energy required to partially overcome intermolecular attractive forces in the solid and causing a phase transition to liquid water. The solution remains at 0 °C until all the ice is melted. Only the amount of water existing as ice changes until the ice disappears. Then the temperature of the water can rise.

Exercise:

Problem:

What feature characterizes the dynamic equilibrium between a liquid and its vapor in a closed container?

Exercise:

Problem:

Identify two common observations indicating some liquids have sufficient vapor pressures to noticeably evaporate?

Solution:

We can see the amount of liquid in an open container decrease and we can smell the vapor of some liquids.

Exercise:

Problem:

Identify two common observations indicating some solids, such as dry ice and mothballs, have vapor pressures sufficient to sublime?

Exercise:

Problem: What is the relationship between the intermolecular forces in a liquid and its vapor pressure?

Solution:

The vapor pressure of a liquid decreases as the strength of its intermolecular forces increases.

Exercise:

Problem: What is the relationship between the intermolecular forces in a solid and its melting temperature?

Exercise:

Problem: Why does spilled gasoline evaporate more rapidly on a hot day than on a cold day?

Solution:

As the temperature increases, the average kinetic energy of the molecules of gasoline increases and so a greater fraction of molecules have sufficient energy to escape from the liquid than at lower temperatures.

Exercise:

Problem:

Carbon tetrachloride, CCl_4 , was once used as a dry cleaning solvent, but is no longer used because it is carcinogenic. At $57.8\text{ }^\circ\text{C}$, the vapor pressure of CCl_4 is 54.0 kPa, and its enthalpy of vaporization is 33.05 kJ/mol. Use this information to estimate the normal boiling point for CCl_4 .

Exercise:

Problem: When is the boiling point of a liquid equal to its normal boiling point?

Solution:

When the pressure of gas above the liquid is exactly 1 atm

Exercise:

Problem: How does the boiling of a liquid differ from its evaporation?

Exercise:

Problem:

Use the information in [\[link\]](#) to estimate the boiling point of water in Denver when the atmospheric pressure is 83.3 kPa.

Solution:

approximately $95\text{ }^\circ\text{C}$

Exercise:

Problem:

A syringe at a temperature of $20\text{ }^\circ\text{C}$ is filled with liquid ether in such a way that there is no space for any vapor. If the temperature is kept constant and the plunger is withdrawn to create a volume that can be occupied by vapor, what would be the approximate pressure of the vapor produced?

Exercise:

Problem: Explain the following observations:

(a) It takes longer to cook an egg in Ft. Davis, Texas (altitude, 5000 feet above sea level) than it does in Boston (at sea level).

(b) Perspiring is a mechanism for cooling the body.

Solution:

(a) At 5000 feet, the atmospheric pressure is lower than at sea level, and water will therefore boil at a lower temperature. This lower temperature will cause the physical and chemical changes involved in cooking the egg to proceed more slowly, and a longer time is required to fully cook the egg. (b) As long as the air

surrounding the body contains less water vapor than the maximum that air can hold at that temperature, perspiration will evaporate, thereby cooling the body by removing the heat of vaporization required to vaporize the water.

Exercise:

Problem: The enthalpy of vaporization of water is larger than its enthalpy of fusion. Explain why.

Exercise:

Problem:

Explain why the molar enthalpies of vaporization of the following substances increase in the order $\text{CH}_4 < \text{C}_2\text{H}_6 < \text{C}_3\text{H}_8$, even though the type of IMF (dispersion) is the same.

Solution:

Dispersion forces increase with molecular mass or size. As the number of atoms composing the molecules in this homologous series increases, so does the extent of intermolecular attraction via dispersion forces and, consequently, the energy required to overcome these forces and vaporize the liquids.

Exercise:

Problem:

Explain why the enthalpies of vaporization of the following substances increase in the order $\text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O}$, even though all three substances have approximately the same molar mass.

Exercise:

Problem:

The enthalpy of vaporization of $\text{CO}_2(l)$ is 9.8 kJ/mol. Would you expect the enthalpy of vaporization of $\text{CS}_2(l)$ to be 28 kJ/mol, 9.8 kJ/mol, or -8.4 kJ/mol? Discuss the plausibility of each of these answers.

Solution:

The boiling point of CS_2 is higher than that of CO_2 partially because of the higher molecular weight of CS_2 ; consequently, the attractive forces are stronger in CS_2 . It would be expected, therefore, that the heat of vaporization would be greater than that of 9.8 kJ/mol for CO_2 . A value of 28 kJ/mol would seem reasonable. A value of -8.4 kJ/mol would indicate a release of energy upon vaporization, which is clearly implausible.

Exercise:

Problem:

The hydrogen fluoride molecule, HF, is more polar than a water molecule, H_2O (for example, has a greater dipole moment), yet the molar enthalpy of vaporization for liquid hydrogen fluoride is lesser than that for water. Explain.

Exercise:

Problem:

Ethyl chloride (boiling point, 13 °C) is used as a local anesthetic. When the liquid is sprayed on the skin, it cools the skin enough to freeze and numb it. Explain the cooling effect of liquid ethyl chloride.

Solution:

The thermal energy (heat) needed to evaporate the liquid is removed from the skin.

Exercise:

Problem: Which contains the compounds listed correctly in order of increasing boiling points?

- (a) $\text{N}_2 < \text{CS}_2 < \text{H}_2\text{O} < \text{KCl}$
- (b) $\text{H}_2\text{O} < \text{N}_2 < \text{CS}_2 < \text{KCl}$
- (c) $\text{N}_2 < \text{KCl} < \text{CS}_2 < \text{H}_2\text{O}$
- (d) $\text{CS}_2 < \text{N}_2 < \text{KCl} < \text{H}_2\text{O}$
- (e) $\text{KCl} < \text{H}_2\text{O} < \text{CS}_2 < \text{N}_2$

Exercise:

Problem: How much heat is required to convert 422 g of liquid H_2O at 23.5°C into steam at 150°C ?

Solution:

1130 kJ

Exercise:

Problem:

Evaporation of sweat requires energy and thus take excess heat away from the body. Some of the water that you drink may eventually be converted into sweat and evaporate. If you drink a 20-ounce bottle of water that had been in the refrigerator at 3.8°C , how much heat is needed to convert all of that water into sweat and then to vapor?? (Note: Your body temperature is 36.6°C . For the purpose of solving this problem, assume that the thermal properties of sweat are the same as for water.)

Exercise:

Problem: Titanium tetrachloride, TiCl_4 , has a melting point of -23.2°C and has a $\Delta H_{\text{fusion}} = 9.37 \text{ kJ/mol}$.

- (a) How much energy is required to melt 263.1 g TiCl_4 ?
 - (b) For TiCl_4 , which will likely have the larger magnitude: ΔH_{fusion} or $\Delta H_{\text{vaporization}}$? Explain your reasoning.
-

Solution:

(a) 13.0 kJ; (b) It is likely that the heat of vaporization will have a larger magnitude since in the case of vaporization the intermolecular interactions have to be completely overcome, while melting weakens or destroys only some of them.

Glossary

boiling point

temperature at which the vapor pressure of a liquid equals the pressure of the gas above it

Clausius-Clapeyron equation

mathematical relationship between the temperature, vapor pressure, and enthalpy of vaporization for a substance

condensation

change from a gaseous to a liquid state

deposition

change from a gaseous state directly to a solid state

dynamic equilibrium

state of a system in which reciprocal processes are occurring at equal rates

freezing

change from a liquid state to a solid state

freezing point

temperature at which the solid and liquid phases of a substance are in equilibrium; see also *melting point*

melting

change from a solid state to a liquid state

melting point

temperature at which the solid and liquid phases of a substance are in equilibrium; see also *freezing point*

normal boiling point

temperature at which a liquid's vapor pressure equals 1 atm (760 torr)

sublimation

change from solid state directly to gaseous state

vapor pressure

(also, equilibrium vapor pressure) pressure exerted by a vapor in equilibrium with a solid or a liquid at a given temperature

vaporization

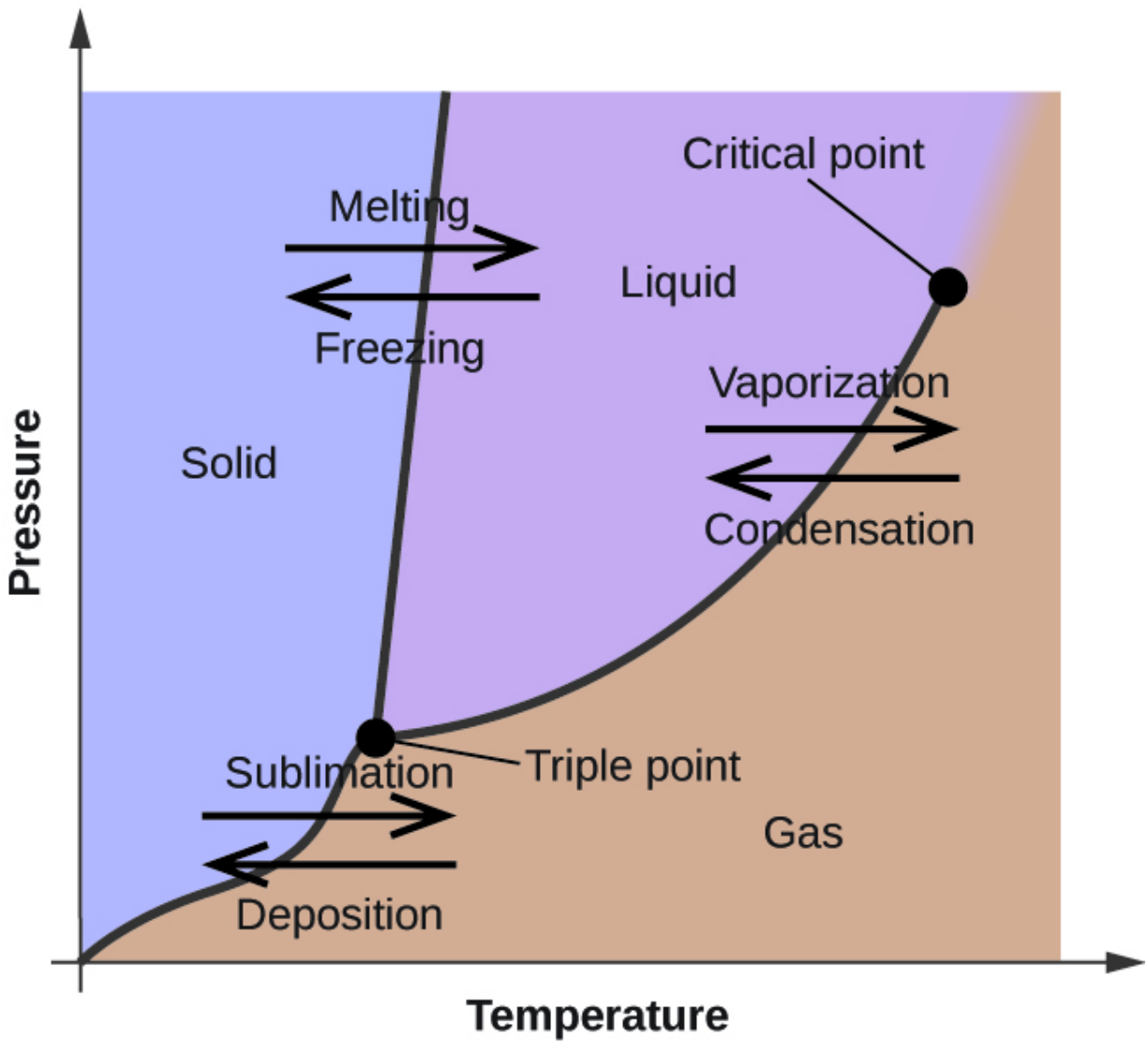
change from liquid state to gaseous state

Phase Diagrams

By the end of this section, you will be able to:

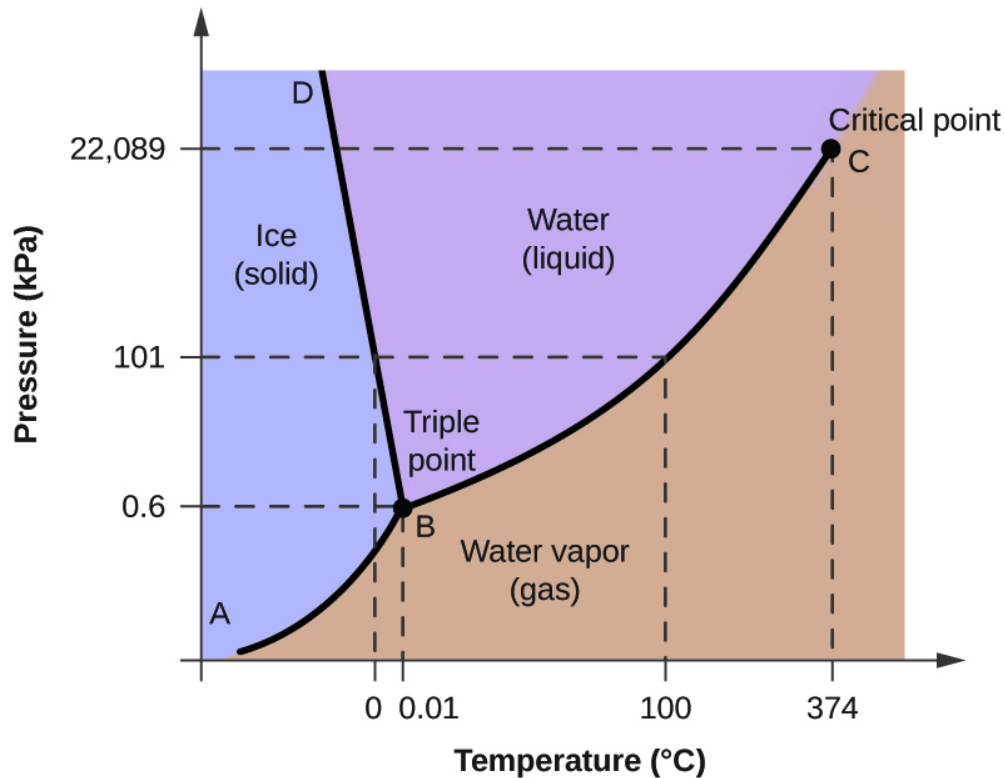
- Explain the construction and use of a typical phase diagram
- Use phase diagrams to identify stable phases at given temperatures and pressures, and to describe phase transitions resulting from changes in these properties
- Describe the supercritical fluid phase of matter

In the previous module, the variation of a liquid's equilibrium vapor pressure with temperature was described. Considering the definition of boiling point, plots of vapor pressure versus temperature represent how the boiling point of the liquid varies with pressure. Also described was the use of heating and cooling curves to determine a substance's melting (or freezing) point. Making such measurements over a wide range of pressures yields data that may be presented graphically as a phase diagram. A **phase diagram** combines plots of pressure versus temperature for the liquid-gas, solid-liquid, and solid-gas phase-transition equilibria of a substance. These diagrams indicate the physical states that exist under specific conditions of pressure and temperature, and also provide the pressure dependence of the phase-transition temperatures (melting points, sublimation points, boiling points). A typical phase diagram for a pure substance is shown in [\[link\]](#).



The physical state of a substance and its phase-transition temperatures are represented graphically in a phase diagram.

To illustrate the utility of these plots, consider the phase diagram for water shown in [\[link\]](#).



The pressure and temperature axes on this phase diagram of water are not drawn to constant scale in order to illustrate several important properties.

We can use the phase diagram to identify the physical state of a sample of water under specified conditions of pressure and temperature. For example, a pressure of 50 kPa and a temperature of -10°C correspond to the region of the diagram labeled “ice.” Under these conditions, water exists only as a solid (ice). A pressure of 50 kPa and a temperature of 50°C correspond to the “water” region—here, water exists only as a liquid. At 25 kPa and 200°C , water exists only in the gaseous state. Note that on the H_2O phase diagram, the pressure and temperature axes are not drawn to a constant scale in order to permit the illustration of several important features as described here.

The curve BC in [\[link\]](#) is the plot of vapor pressure versus temperature as described in the previous module of this chapter. This “liquid-vapor” curve

separates the liquid and gaseous regions of the phase diagram and provides the boiling point for water at any pressure. For example, at 1 atm, the boiling point is 100 °C. Notice that the liquid-vapor curve terminates at a temperature of 374 °C and a pressure of 218 atm, indicating that water cannot exist as a liquid above this temperature, regardless of the pressure. The physical properties of water under these conditions are intermediate between those of its liquid and gaseous phases. This unique state of matter is called a supercritical fluid, a topic that will be described in the next section of this module.

The solid-vapor curve, labeled AB in [\[link\]](#), indicates the temperatures and pressures at which ice and water vapor are in equilibrium. These temperature-pressure data pairs correspond to the sublimation, or deposition, points for water. If we could zoom in on the solid-gas line in [\[link\]](#), we would see that ice has a vapor pressure of about 0.20 kPa at −10 °C. Thus, if we place a frozen sample in a vacuum with a pressure less than 0.20 kPa, ice will sublime. This is the basis for the “freeze-drying” process often used to preserve foods, such as the ice cream shown in [\[link\]](#).



Freeze-dried foods, like this ice cream, are dehydrated by sublimation at pressures below the triple point for water. (credit: "lwao"/Flickr)

The solid-liquid curve labeled BD shows the temperatures and pressures at which ice and liquid water are in equilibrium, representing the melting/freezing points for water. Note that this curve exhibits a slight negative slope (greatly exaggerated for clarity), indicating that the melting point for water decreases slightly as pressure increases. Water is an unusual substance in this regard, as most substances exhibit an increase in melting point with increasing pressure. This behavior is partly responsible for the movement of glaciers, like the one shown in [\[link\]](#). The bottom of a glacier experiences an immense pressure due to its weight that can melt some of the ice, forming a layer of liquid water on which the glacier may more easily slide.



The immense pressures beneath glaciers result in partial melting to produce a layer of water that provides lubrication to assist glacial movement. This satellite photograph shows the advancing edge of the Perito Moreno glacier in Argentina. (credit: NASA)

The point of intersection of all three curves is labeled B in [\[link\]](#). At the pressure and temperature represented by this point, all three phases of water coexist in equilibrium. This temperature-pressure data pair is called the **triple point**. At pressures lower than the triple point, water cannot exist as a liquid, regardless of the temperature.

Example:

Determining the State of Water

Using the phase diagram for water given in [\[link\]](#), determine the state of water at the following temperatures and pressures:

- (a) $-10\text{ }^{\circ}\text{C}$ and 50 kPa
- (b) $25\text{ }^{\circ}\text{C}$ and 90 kPa
- (c) $50\text{ }^{\circ}\text{C}$ and 40 kPa
- (d) $80\text{ }^{\circ}\text{C}$ and 5 kPa
- (e) $-10\text{ }^{\circ}\text{C}$ and 0.3 kPa
- (f) $50\text{ }^{\circ}\text{C}$ and 0.3 kPa

Solution

Using the phase diagram for water, we can determine that the state of water at each temperature and pressure given are as follows: (a) solid; (b) liquid; (c) liquid; (d) gas; (e) solid; (f) gas.

Check Your Learning

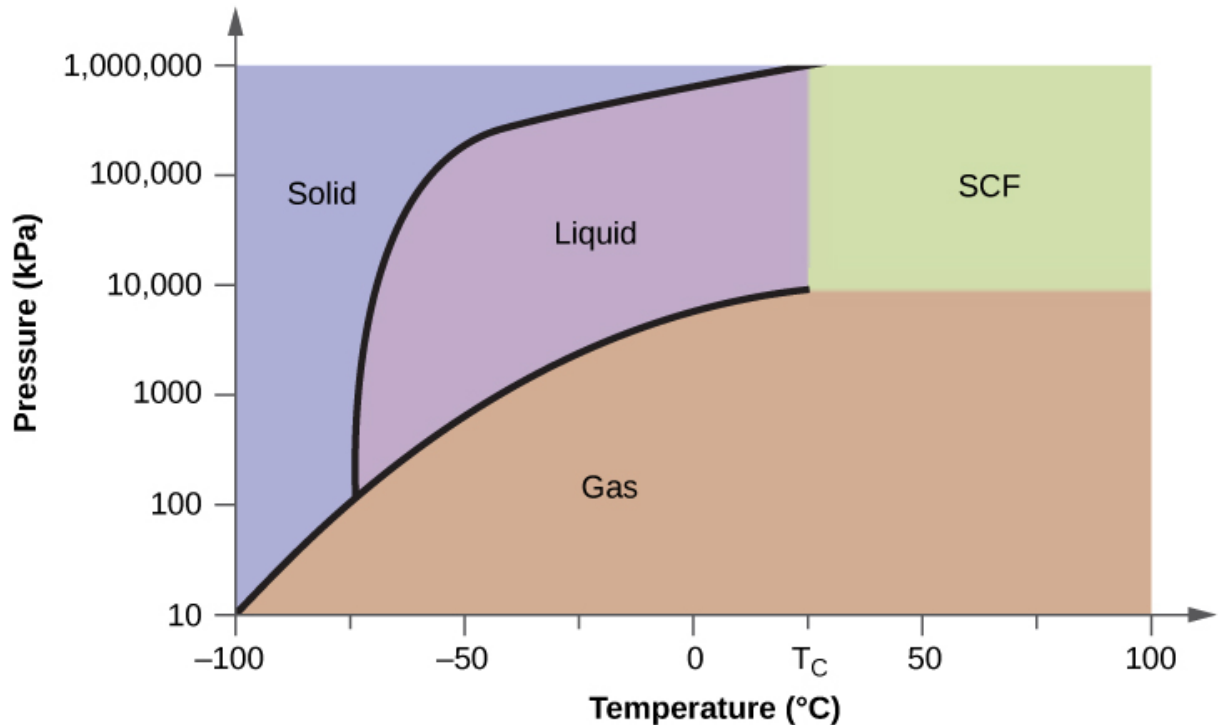
What phase changes can water undergo as the temperature changes if the pressure is held at 0.3 kPa? If the pressure is held at 50 kPa?

Note:

Answer:

At 0.3 kPa: $s \longrightarrow g$ at $-58\text{ }^{\circ}\text{C}$. At 50 kPa: $s \longrightarrow l$ at $0\text{ }^{\circ}\text{C}$, $l \longrightarrow g$ at $78\text{ }^{\circ}\text{C}$

Consider the phase diagram for carbon dioxide shown in [\[link\]](#) as another example. The solid-liquid curve exhibits a positive slope, indicating that the melting point for CO_2 increases with pressure as it does for most substances (water being a notable exception as described previously). Notice that the triple point is well above 1 atm, indicating that carbon dioxide cannot exist as a liquid under ambient pressure conditions. Instead, cooling gaseous carbon dioxide at 1 atm results in its deposition into the solid state. Likewise, solid carbon dioxide does not melt at 1 atm pressure but instead sublimates to yield gaseous CO_2 . Finally, notice that the critical point for carbon dioxide is observed at a relatively modest temperature and pressure in comparison to water.



The pressure and temperature axes on this phase diagram of carbon dioxide are not drawn to constant scale in order to illustrate several important properties.

Example:

Determining the State of Carbon Dioxide

Using the phase diagram for carbon dioxide shown in [\[link\]](#), determine the state of CO_2 at the following temperatures and pressures:

- (a) -30°C and 2000 kPa
- (b) -60°C and 1000 kPa
- (c) -60°C and 100 kPa
- (d) 20°C and 1500 kPa
- (e) 0°C and 100 kPa
- (f) 20°C and 100 kPa

Solution

Using the phase diagram for carbon dioxide provided, we can determine that the state of CO₂ at each temperature and pressure given are as follows: (a) liquid; (b) solid; (c) gas; (d) liquid; (e) gas; (f) gas.

Check Your Learning

Determine the phase changes carbon dioxide undergoes when its temperature is varied, thus holding its pressure constant at 1500 kPa? At 500 kPa? At what approximate temperatures do these phase changes occur?

Note:

Answer:

at 1500 kPa: s \rightarrow l at $-45\text{ }^{\circ}\text{C}$, l \rightarrow g at $-10\text{ }^{\circ}\text{C}$;

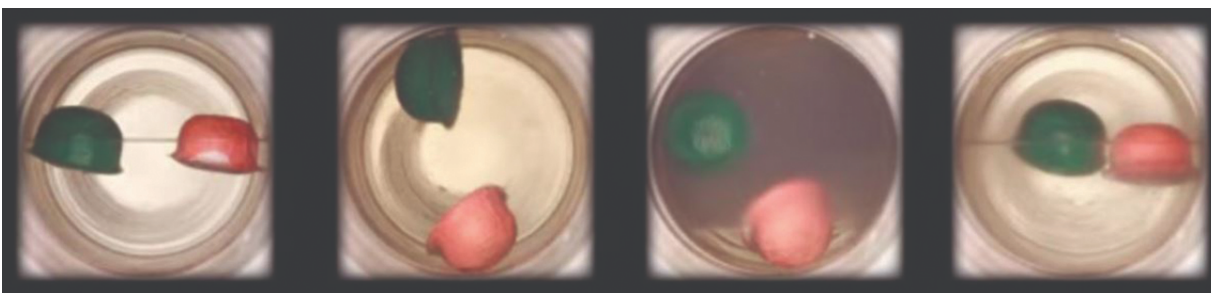
at 500 kPa: s \rightarrow g at $-58\text{ }^{\circ}\text{C}$

Supercritical Fluids

If we place a sample of water in a sealed container at $25\text{ }^{\circ}\text{C}$, remove the air, and let the vaporization-condensation equilibrium establish itself, we are left with a mixture of liquid water and water vapor at a pressure of 0.03 atm. A distinct boundary between the more dense liquid and the less dense gas is clearly observed. As we increase the temperature, the pressure of the water vapor increases, as described by the liquid-gas curve in the phase diagram for water ([\[link\]](#)), and a two-phase equilibrium of liquid and gaseous phases remains. At a temperature of $374\text{ }^{\circ}\text{C}$, the vapor pressure has risen to 218 atm, and any further increase in temperature results in the disappearance of the boundary between liquid and vapor phases. All of the water in the container is now present in a single phase whose physical properties are intermediate between those of the gaseous and liquid states. This phase of matter is called a **supercritical fluid**, and the temperature and pressure above which this phase exists is the **critical point** ([\[link\]](#)). Above its critical temperature, a gas cannot be liquefied no matter how much

pressure is applied. The pressure required to liquefy a gas at its critical temperature is called the critical pressure. The critical temperatures and critical pressures of some common substances are given in [\[link\]](#).

Substance	Critical Temperature (K)	Critical Pressure (atm)
hydrogen	33.2	12.8
nitrogen	126.0	33.5
oxygen	154.3	49.7
carbon dioxide	304.2	73.0
ammonia	405.5	111.5
sulfur dioxide	430.3	77.7
water	647.1	217.7



(a) A sealed container of liquid carbon dioxide slightly below its critical point is heated, resulting in (b) the formation of the supercritical fluid phase. Cooling the supercritical fluid lowers its temperature and pressure below the critical point, resulting in the reestablishment of separate liquid and gaseous phases (c and d). Colored floats illustrate differences in density between the liquid, gaseous, and supercritical fluid states. (credit: modification of work by “mrmrobin”/YouTube)

Note:



Observe the [liquid-to-supercritical fluid transition](#) for carbon dioxide.

Like a gas, a supercritical fluid will expand and fill a container, but its density is much greater than typical gas densities, typically being close to those for liquids. Similar to liquids, these fluids are capable of dissolving nonvolatile solutes. They exhibit essentially no surface tension and very low viscosities, however, so they can more effectively penetrate very small openings in a solid mixture and remove soluble components. These properties make supercritical fluids extremely useful solvents for a wide range of applications. For example, supercritical carbon dioxide has become a very popular solvent in the food industry, being used to decaffeinate coffee, remove fats from potato chips, and extract flavor and fragrance compounds from citrus oils. It is nontoxic, relatively inexpensive, and not

considered to be a pollutant. After use, the CO_2 can be easily recovered by reducing the pressure and collecting the resulting gas.

Example:

The Critical Temperature of Carbon Dioxide

If we shake a carbon dioxide fire extinguisher on a cool day ($18\text{ }^\circ\text{C}$), we can hear liquid CO_2 sloshing around inside the cylinder. However, the same cylinder appears to contain no liquid on a hot summer day ($35\text{ }^\circ\text{C}$). Explain these observations.

Solution

On the cool day, the temperature of the CO_2 is below the critical temperature of CO_2 , 304 K or $31\text{ }^\circ\text{C}$ ([link](#)), so liquid CO_2 is present in the cylinder. On the hot day, the temperature of the CO_2 is greater than its critical temperature of $31\text{ }^\circ\text{C}$. Above this temperature no amount of pressure can liquefy CO_2 so no liquid CO_2 exists in the fire extinguisher.

Check Your Learning

Ammonia can be liquefied by compression at room temperature; oxygen cannot be liquefied under these conditions. Why do the two gases exhibit different behavior?

Note:

Answer:

The critical temperature of ammonia is 405.5 K , which is higher than room temperature. The critical temperature of oxygen is below room temperature; thus oxygen cannot be liquefied at room temperature.

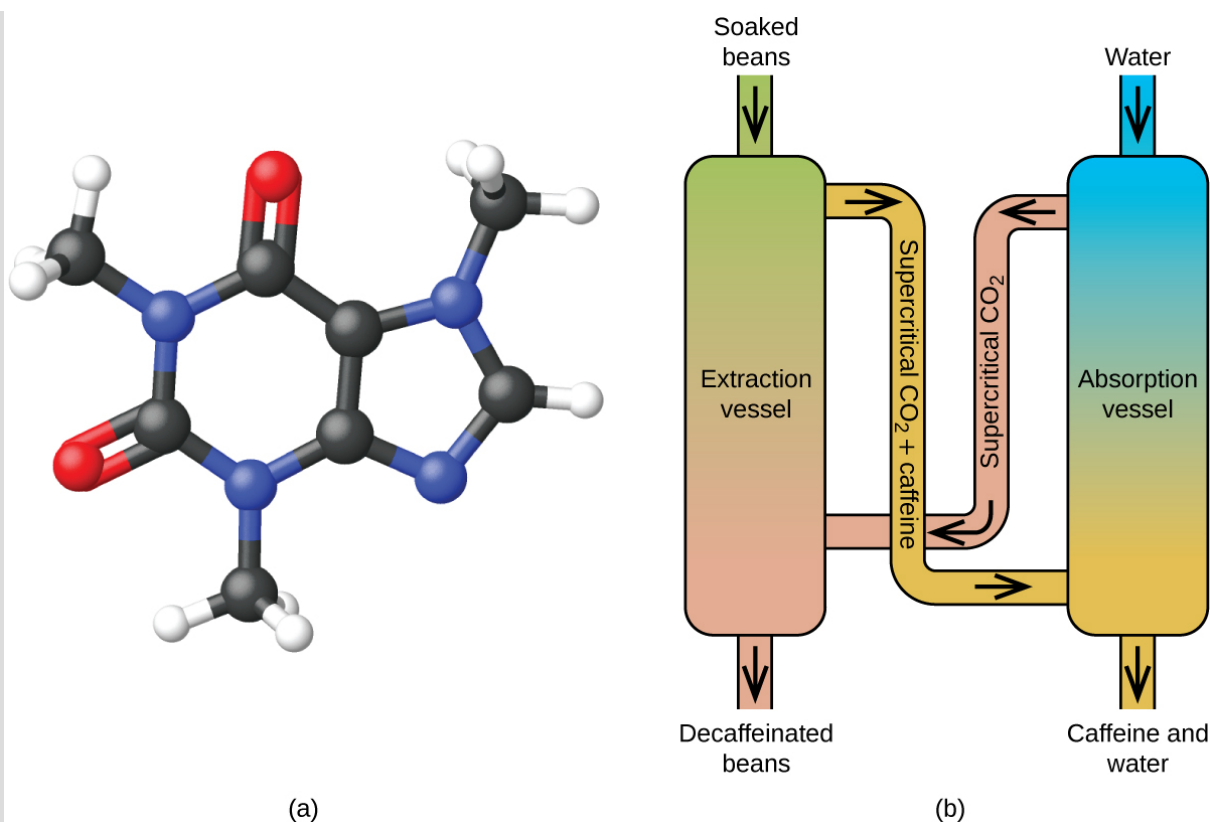
Note:

Decaffeinating Coffee Using Supercritical CO_2

Coffee is the world's second most widely traded commodity, following only petroleum. Across the globe, people love coffee's aroma and taste. Many of us also depend on one component of coffee—caffeine—to help us get going in the morning or stay alert in the afternoon. But late in the day, coffee's stimulant effect can keep you from sleeping, so you may choose to drink decaffeinated coffee in the evening.

Since the early 1900s, many methods have been used to decaffeinate coffee. All have advantages and disadvantages, and all depend on the physical and chemical properties of caffeine. Because caffeine is a somewhat polar molecule, it dissolves well in water, a polar liquid. However, since many of the other 400-plus compounds that contribute to coffee's taste and aroma also dissolve in H_2O , hot water decaffeination processes can also remove some of these compounds, adversely affecting the smell and taste of the decaffeinated coffee. Dichloromethane (CH_2Cl_2) and ethyl acetate ($\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$) have similar polarity to caffeine, and are therefore very effective solvents for caffeine extraction, but both also remove some flavor and aroma components, and their use requires long extraction and cleanup times. Because both of these solvents are toxic, health concerns have been raised regarding the effect of residual solvent remaining in the decaffeinated coffee.

Supercritical fluid extraction using carbon dioxide is now being widely used as a more effective and environmentally friendly decaffeination method ([\[link\]](#)). At temperatures above 304.2 K and pressures above 7376 kPa, CO_2 is a supercritical fluid, with properties of both gas and liquid. Like a gas, it penetrates deep into the coffee beans; like a liquid, it effectively dissolves certain substances. Supercritical carbon dioxide extraction of steamed coffee beans removes 97–99% of the caffeine, leaving coffee's flavor and aroma compounds intact. Because CO_2 is a gas under standard conditions, its removal from the extracted coffee beans is easily accomplished, as is the recovery of the caffeine from the extract. The caffeine recovered from coffee beans via this process is a valuable product that can be used subsequently as an additive to other foods or drugs.



(a) Caffeine molecules have both polar and nonpolar regions, making it soluble in solvents of varying polarities. (b) The schematic shows a typical decaffeination process involving supercritical carbon dioxide.

Key Concepts and Summary

The temperature and pressure conditions at which a substance exists in solid, liquid, and gaseous states are summarized in a phase diagram for that substance. Phase diagrams are combined plots of three pressure-temperature equilibrium curves: solid-liquid, liquid-gas, and solid-gas. These curves represent the relationships between phase-transition temperatures and pressures. The point of intersection of all three curves represents the substance's triple point—the temperature and pressure at which all three phases are in equilibrium. At pressures below the triple point, a substance

cannot exist in the liquid state, regardless of its temperature. The terminus of the liquid-gas curve represents the substance's critical point, the pressure and temperature above which a liquid phase cannot exist.

Chemistry End of Chapter Exercises

Exercise:

Problem:

From the phase diagram for water ([link](#)), determine the state of water at:

- (a) 35 °C and 85 kPa
- (b) -15 °C and 40 kPa
- (c) -15 °C and 0.1 kPa
- (d) 75 °C and 3 kPa
- (e) 40 °C and 0.1 kPa
- (f) 60 °C and 50 kPa

Exercise:

Problem:

What phase changes will take place when water is subjected to varying pressure at a constant temperature of 0.005 °C? At 40 °C? At -40 °C?

Solution:

At low pressures and 0.005 °C, the water is a gas. As the pressure increases to 4.6 torr, the water becomes a solid; as the pressure increases still more, it becomes a liquid. At 40 °C, water at low pressure is a vapor; at pressures higher than about 75 torr, it converts into a liquid. At -40 °C, water goes from a gas to a solid as the pressure increases above very low values.

Exercise:**Problem:**

Pressure cookers allow food to cook faster because the higher pressure inside the pressure cooker increases the boiling temperature of water. A particular pressure cooker has a safety valve that is set to vent steam if the pressure exceeds 3.4 atm. What is the approximate maximum temperature that can be reached inside this pressure cooker? Explain your reasoning.

Exercise:**Problem:**

From the phase diagram for carbon dioxide in [\[link\]](#), determine the state of CO₂ at:

- (a) 20 °C and 1000 kPa
- (b) 10 °C and 2000 kPa
- (c) 10 °C and 100 kPa
- (d) -40 °C and 500 kPa
- (e) -80 °C and 1500 kPa
- (f) -80 °C and 10 kPa

Solution:

(a) gas; (b) gas; (c) gas; (d) gas; (e) solid; (f) gas

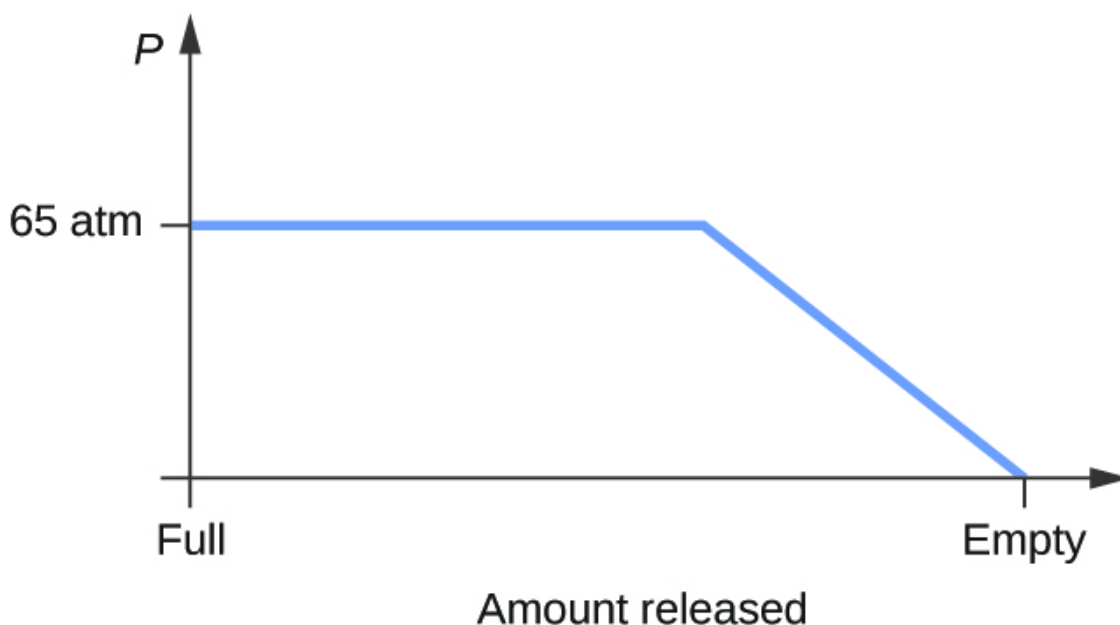
Exercise:

Problem:

Determine the phase changes that carbon dioxide undergoes as the pressure changes if the temperature is held at $-50\text{ }^{\circ}\text{C}$? If the temperature is held at $-40\text{ }^{\circ}\text{C}$? At $20\text{ }^{\circ}\text{C}$? (See the phase diagram in [\[link\]](#).)

Exercise:**Problem:**

Consider a cylinder containing a mixture of liquid carbon dioxide in equilibrium with gaseous carbon dioxide at an initial pressure of 65 atm and a temperature of $20\text{ }^{\circ}\text{C}$. Sketch a plot depicting the change in the cylinder pressure with time as gaseous carbon dioxide is released at constant temperature.

Solution:**Exercise:**

Problem:

Dry ice, $\text{CO}_2(\text{s})$, does not melt at atmospheric pressure. It sublimates at a temperature of $-78\text{ }^\circ\text{C}$. What is the lowest pressure at which $\text{CO}_2(\text{s})$ will melt to give $\text{CO}_2(\text{l})$? At approximately what temperature will this occur? (See [\[link\]](#) for the phase diagram.)

Exercise:**Problem:**

If a severe storm results in the loss of electricity, it may be necessary to use a clothesline to dry laundry. In many parts of the country in the dead of winter, the clothes will quickly freeze when they are hung on the line. If it does not snow, will they dry anyway? Explain your answer.

Solution:

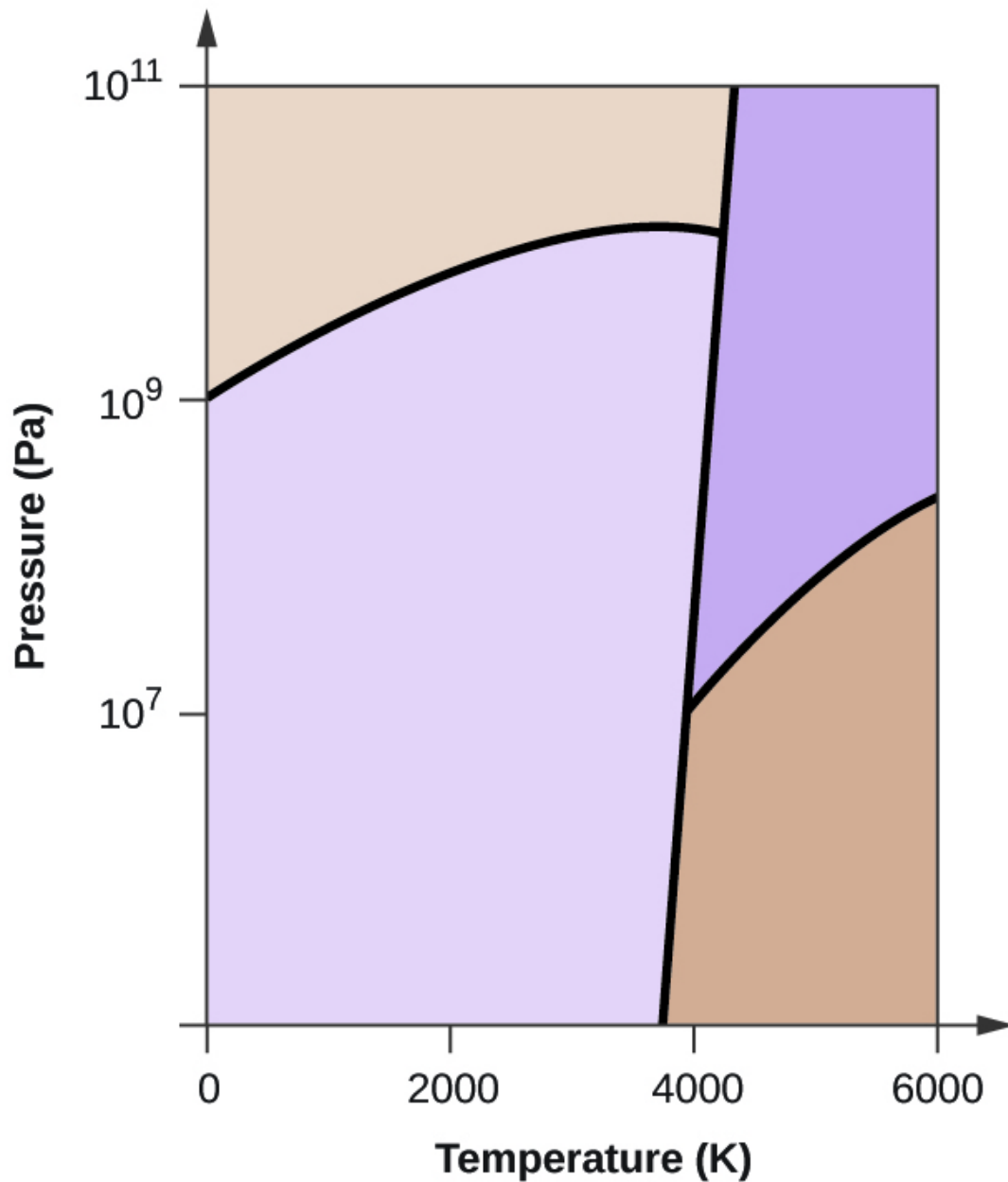
Yes, ice will sublime, although it may take it several days. Ice has a small vapor pressure, and some ice molecules form gas and escape from the ice crystals. As time passes, more and more solid converts to gas until eventually the clothes are dry.

Exercise:**Problem:**

Is it possible to liquefy nitrogen at room temperature (about $25\text{ }^\circ\text{C}$)? Is it possible to liquefy sulfur dioxide at room temperature? Explain your answers.

Exercise:**Problem:**

Elemental carbon has one gas phase, one liquid phase, and two different solid phases, as shown in the phase diagram:



- (a) On the phase diagram, label the gas and liquid regions.
- (b) Graphite is the most stable phase of carbon at normal conditions. On the phase diagram, label the graphite phase.
- (c) If graphite at normal conditions is heated to 2500 K while the pressure is increased to 10^{10} Pa, it is converted into diamond. Label the diamond phase.

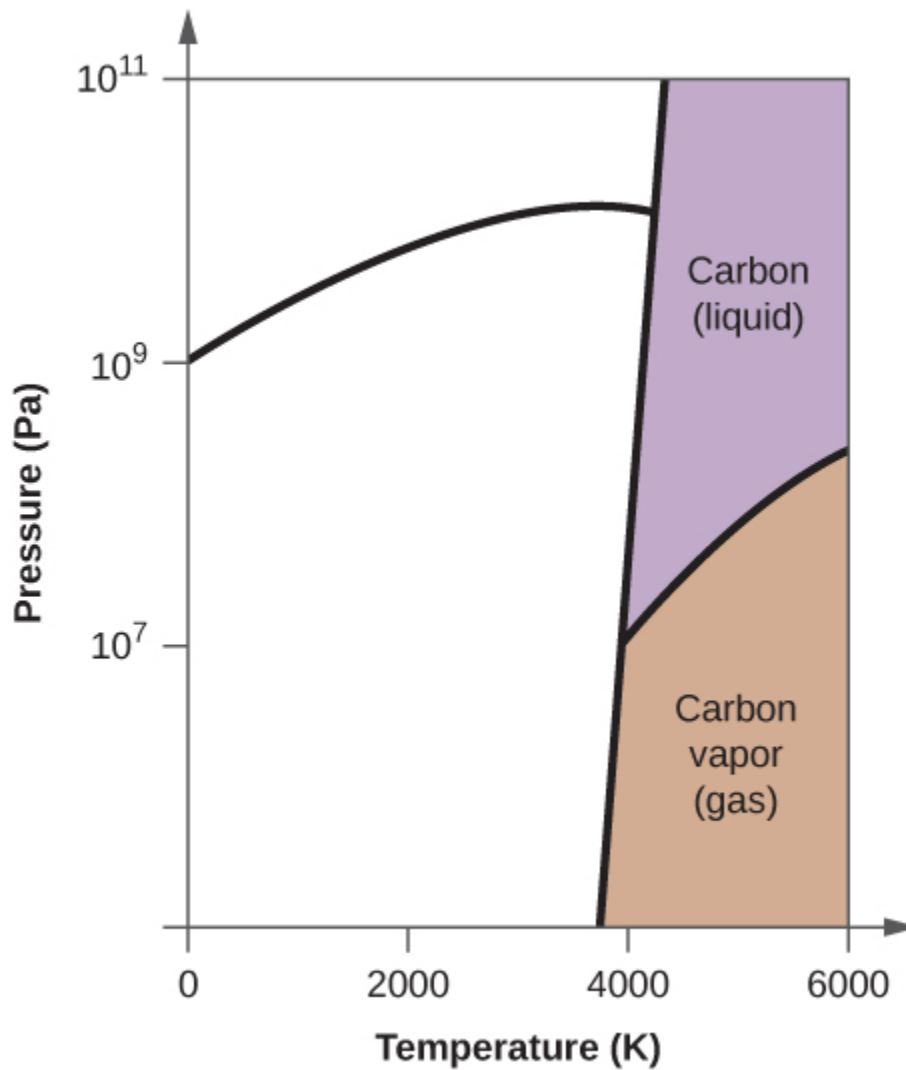
(d) Circle each triple point on the phase diagram.

(e) In what phase does carbon exist at 5000 K and 10^8 Pa?

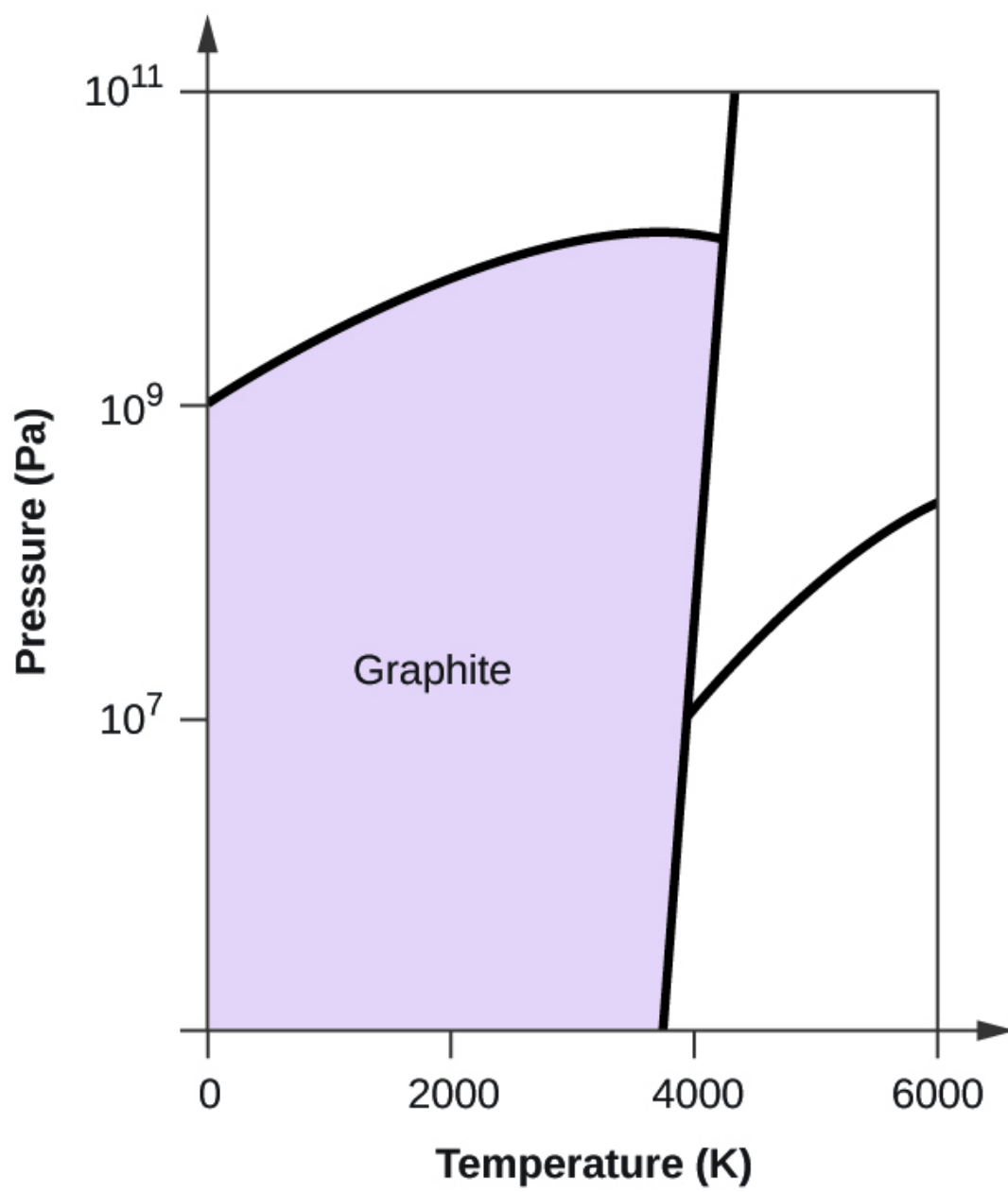
(f) If the temperature of a sample of carbon increases from 3000 K to 5000 K at a constant pressure of 10^6 Pa, which phase transition occurs, if any?

Solution:

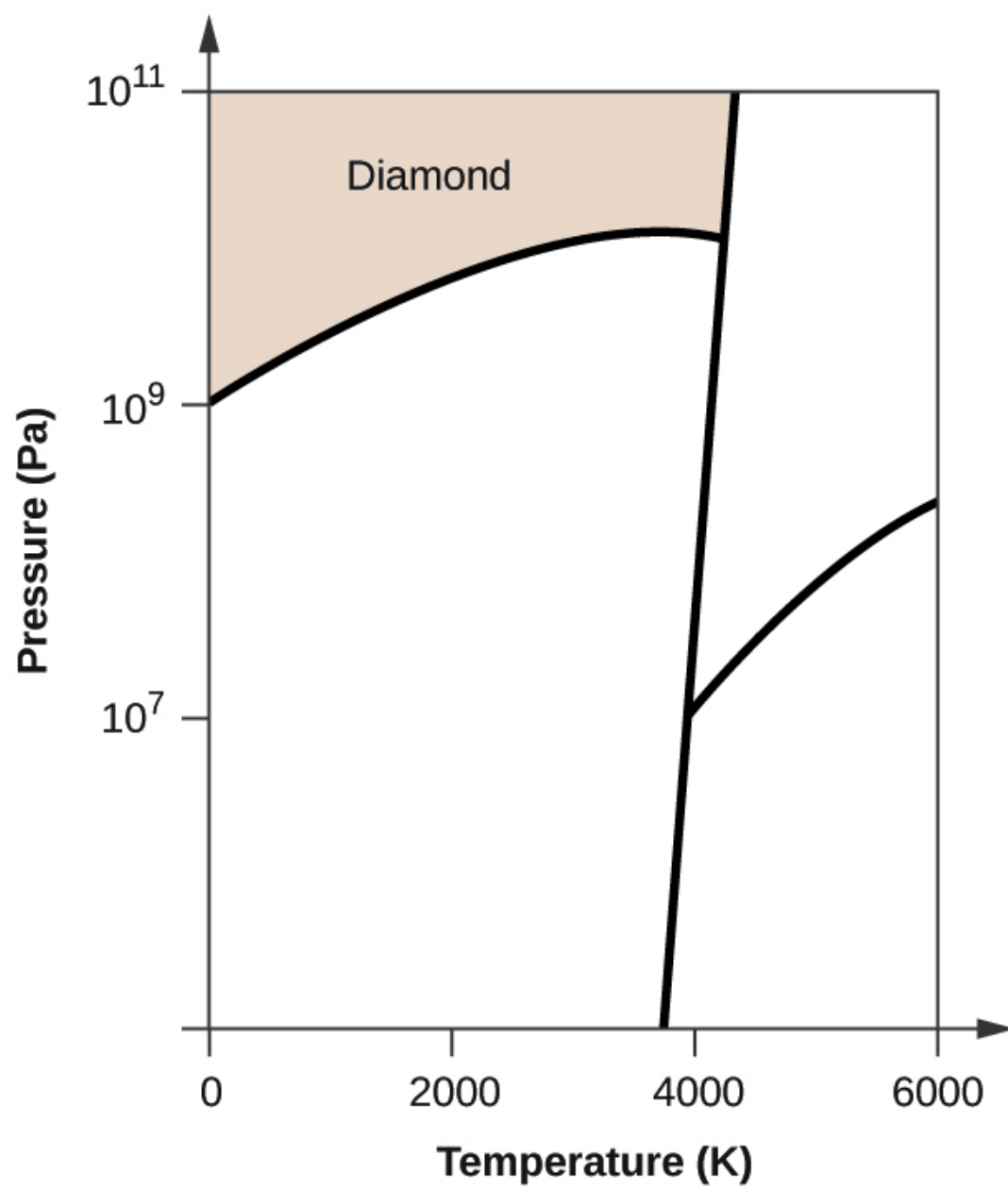
(a)



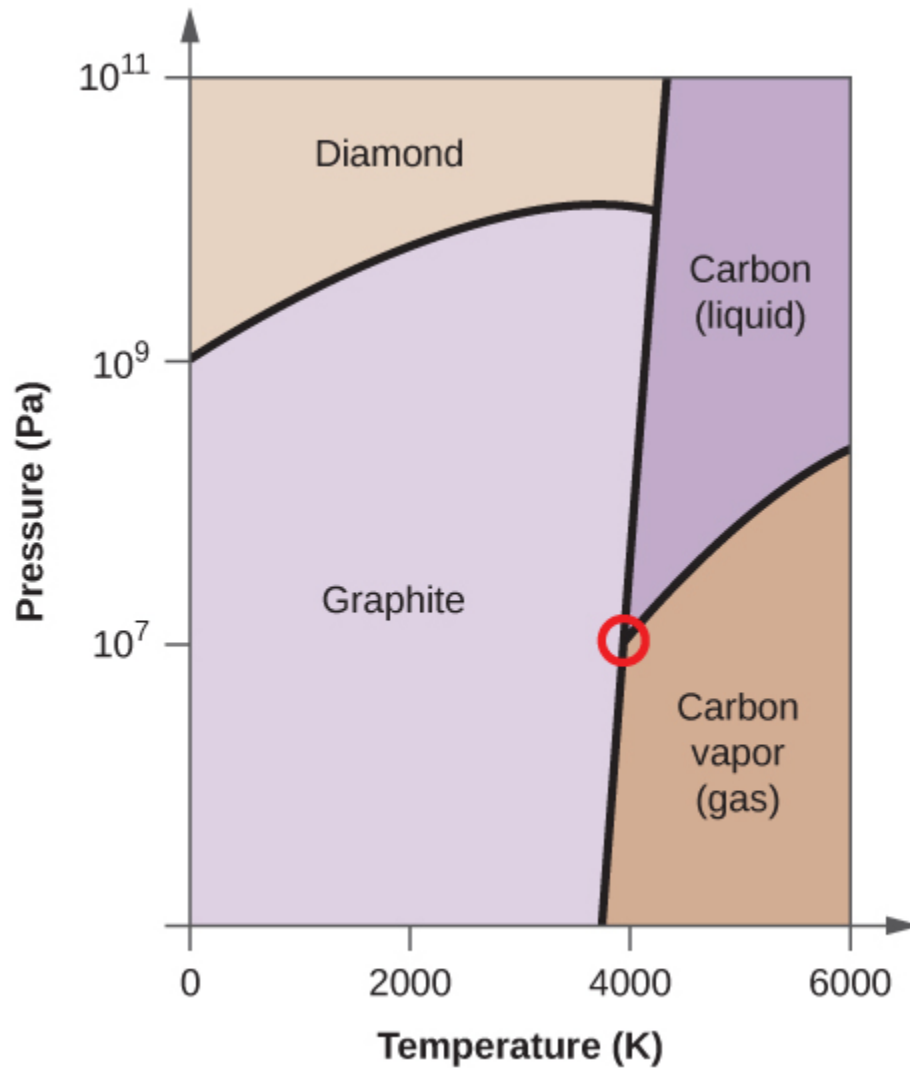
(b)



(c)



(d)



(e) liquid phase (f) sublimation

Glossary

critical point

temperature and pressure above which a gas cannot be condensed into a liquid

phase diagram

pressure-temperature graph summarizing conditions under which the phases of a substance can exist

supercritical fluid

substance at a temperature and pressure higher than its critical point; exhibits properties intermediate between those of gaseous and liquid states

triple point

temperature and pressure at which the vapor, liquid, and solid phases of a substance are in equilibrium

Introduction

class="introduction"

- Chemical Reaction Rates
- Factors Affecting Reaction Rates
- Rate Laws
- Integrated Rate Laws
- Collision Theory
- Reaction Mechanisms
- Catalysis

An agama
lizard
basks in
the sun. As
its body
warms, the
chemical
reactions
of its
metabolis
m speed
up.



The lizard in the photograph is not simply enjoying the sunshine or working on its tan. The heat from the sun's rays is critical to the lizard's survival. A warm lizard can move faster than a cold one because the chemical reactions that allow its muscles to move occur more rapidly at higher temperatures. In the absence of warmth, the lizard is an easy meal for predators.

From baking a cake to determining the useful lifespan of a bridge, rates of chemical reactions play important roles in our understanding of processes that involve chemical changes. When planning to run a chemical reaction, we should ask at least two questions. The first is: "Will the reaction produce the desired products in useful quantities?" The second question is: "How rapidly will the reaction occur?" A reaction that takes 50 years to produce a product is about as useful as one that never gives a product at all. A third question is often asked when investigating reactions in greater detail: "What specific molecular-level processes take place as the reaction occurs?" Knowing the answer to this question is of practical importance when the yield or rate of a reaction needs to be controlled.

The study of chemical kinetics concerns the second and third questions—that is, the rate at which a reaction yields products and the molecular-scale means by which a reaction occurs. In this chapter, we will examine the factors that influence the rates of chemical reactions, the mechanisms by which reactions proceed, and the quantitative techniques used to determine and describe the rate at which reactions occur.

Molarity

By the end of this section, you will be able to:

- Describe the fundamental properties of solutions
- Calculate solution concentrations using molarity
- Perform dilution calculations using the dilution equation

In preceding sections, we focused on the composition of substances: samples of matter that contain only one type of element or compound. However, mixtures—samples of matter containing two or more substances physically combined—are more commonly encountered in nature than are pure substances. Similar to a pure substance, the relative composition of a mixture plays an important role in determining its properties. The relative amount of oxygen in a planet’s atmosphere determines its ability to sustain aerobic life. The relative amounts of iron, carbon, nickel, and other elements in steel (a mixture known as an “alloy”) determine its physical strength and resistance to corrosion. The relative amount of the active ingredient in a medicine determines its effectiveness in achieving the desired pharmacological effect. The relative amount of sugar in a beverage determines its sweetness (see [\[link\]](#)). In this section, we will describe one of the most common ways in which the relative compositions of mixtures may be quantified.



Sugar is one of many components in the complex mixture known as coffee. The amount of sugar in a given amount of coffee is an important determinant of the beverage's sweetness. (credit: Jane Whitney)

Solutions

We have previously defined solutions as homogeneous mixtures, meaning that the composition of the mixture (and therefore its properties) is uniform throughout its entire volume. Solutions occur frequently in nature and have also been implemented in many forms of manmade technology. We will explore a more thorough treatment of solution properties in the chapter on solutions and colloids, but here we will introduce some of the basic properties of solutions.

The relative amount of a given solution component is known as its **concentration**. Often, though not always, a solution contains one component with a concentration that is significantly greater than that of all other components. This component is called the **solvent** and may be viewed as the medium in which the other components are dispersed, or **dissolved**. Solutions in which water is the solvent are, of course, very common on our planet. A solution in which water is the solvent is called an **aqueous solution**.

A **solute** is a component of a solution that is typically present at a much lower concentration than the solvent. Solute concentrations are often described with qualitative terms such as **dilute** (of relatively low concentration) and **concentrated** (of relatively high concentration).

Concentrations may be quantitatively assessed using a wide variety of measurement units, each convenient for particular applications. **Molarity (M)** is a useful concentration unit for many applications in chemistry. Molarity is defined as the number of moles of solute in exactly 1 liter (1 L) of the solution:

Equation:

$$M = \frac{\text{mol solute}}{\text{L solution}}$$

Example:

Calculating Molar Concentrations

A 355-mL soft drink sample contains 0.133 mol of sucrose (table sugar). What is the molar concentration of sucrose in the beverage?

Solution

Since the molar amount of solute and the volume of solution are both given, the molarity can be calculated using the definition of molarity. Per this definition, the solution volume must be converted from mL to L:

Equation:

$$M = \frac{\text{mol solute}}{\text{L solution}} = \frac{0.133 \text{ mol}}{355 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}} = 0.375 M$$

Check Your Learning

A teaspoon of table sugar contains about 0.01 mol sucrose. What is the molarity of sucrose if a teaspoon of sugar has been dissolved in a cup of tea with a volume of 200 mL?

Note:**Answer:**

0.05 M

Example:**Deriving Moles and Volumes from Molar Concentrations**

How much sugar (mol) is contained in a modest sip (~10 mL) of the soft drink from [\[link\]](#)?

Solution

In this case, we can rearrange the definition of molarity to isolate the quantity sought, moles of sugar. We then substitute the value for molarity that we derived in [\[link\]](#), 0.375 M:

Equation:

$$M = \frac{\text{mol solute}}{\text{L solution}}$$
$$\text{mol solute} = M \times \text{L solution}$$

$$\text{mol solute} = 0.375 \frac{\text{mol sugar}}{\text{L}} \times \left(10 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}\right) = 0.004 \text{ mol sugar}$$

Check Your Learning

What volume (mL) of the sweetened tea described in [\[link\]](#) contains the same amount of sugar (mol) as 10 mL of the soft drink in this example?

Note:

Answer:

80 mL

Example:

Calculating Molar Concentrations from the Mass of Solute

Distilled white vinegar ([\[link\]](#)) is a solution of acetic acid, $\text{CH}_3\text{CO}_2\text{H}$, in water. A 0.500-L vinegar solution contains 25.2 g of acetic acid. What is the concentration of the acetic acid solution in units of molarity?



Distilled white vinegar is a solution of acetic acid in water.

Solution

As in previous examples, the definition of molarity is the primary equation used to calculate the quantity sought. In this case, the mass of solute is provided instead of its molar amount, so we must use the solute's molar mass to obtain the amount of solute in moles:

Equation:

$$M = \frac{\text{mol solute}}{\text{L solution}} = \frac{25.2 \text{ g CH}_3\text{CO}_2\text{H} \times \frac{1 \text{ mol CH}_3\text{CO}_2\text{H}}{60.052 \text{ g CH}_3\text{CO}_2\text{H}}}{0.500 \text{ L solution}} = 0.839 M$$

Equation:

$$M = \frac{\text{mol solute}}{\text{L solution}} = 0.839 M$$

$$M = \frac{0.839 \text{ mol solute}}{1.00 \text{ L solution}}$$

Check Your Learning

Calculate the molarity of 6.52 g of CoCl_2 (128.9 g/mol) dissolved in an aqueous solution with a total volume of 75.0 mL.

Note:

Answer:

0.674 M

Example:

Determining the Mass of Solute in a Given Volume of Solution

How many grams of NaCl are contained in 0.250 L of a 5.30-M solution?

Solution

The volume and molarity of the solution are specified, so the amount (mol) of solute is easily computed as demonstrated in [\[link\]](#):

Equation:

$$M = \frac{\text{mol solute}}{\text{L solution}}$$

$$\text{mol solute} = M \times \text{L solution}$$

$$\text{mol solute} = 5.30 \frac{\text{mol NaCl}}{\text{L}} \times 0.250 \text{ L} = 1.325 \text{ mol NaCl}$$

Finally, this molar amount is used to derive the mass of NaCl:

Equation:

$$1.325 \text{ mol NaCl} \times \frac{58.44 \text{ g NaCl}}{\text{mol NaCl}} = 77.4 \text{ g NaCl}$$

Check Your Learning

How many grams of CaCl_2 (110.98 g/mol) are contained in 250.0 mL of a 0.200-M solution of calcium chloride?

Note:

Answer:

5.55 g CaCl₂

When performing calculations stepwise, as in [\[link\]](#), it is important to refrain from rounding any intermediate calculation results, which can lead to rounding errors in the final result. In [\[link\]](#), the molar amount of NaCl computed in the first step, 1.325 mol, would be properly rounded to 1.32 mol if it were to be reported; however, although the last digit (5) is not significant, it must be retained as a guard digit in the intermediate calculation. If we had not retained this guard digit, the final calculation for the mass of NaCl would have been 77.1 g, a difference of 0.3 g.

In addition to retaining a guard digit for intermediate calculations, we can also avoid rounding errors by performing computations in a single step (see [\[link\]](#)). This eliminates intermediate steps so that only the final result is rounded.

Example:

Determining the Volume of Solution Containing a Given Mass of Solute

In [\[link\]](#), we found the typical concentration of vinegar to be 0.839 M. What volume of vinegar contains 75.6 g of acetic acid?

Solution

First, use the molar mass to calculate moles of acetic acid from the given mass:

Equation:

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} = \text{mol solute}$$

Then, use the molarity of the solution to calculate the volume of solution containing this molar amount of solute:

Equation:

$$\text{mol solute} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution}$$

Combining these two steps into one yields:

Equation:

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution}$$

Equation:

$$75.6 \text{ g CH}_3\text{CO}_2\text{H} \left(\frac{\text{mol CH}_3\text{CO}_2\text{H}}{60.05 \text{ g}} \right) \left(\frac{\text{L solution}}{0.839 \text{ mol CH}_3\text{CO}_2\text{H}} \right) = 1.50 \text{ L solution}$$

Check Your Learning

What volume of a 1.50-M KBr solution contains 66.0 g KBr?

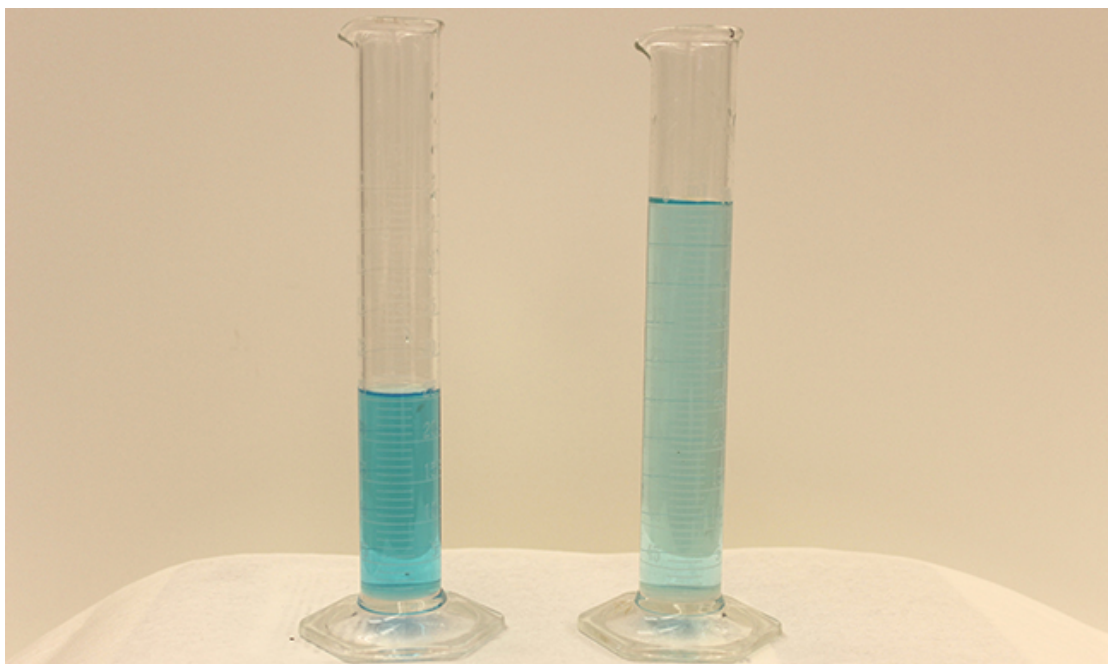
Note:

Answer:

0.370 L

Dilution of Solutions

Dilution is the process whereby the concentration of a solution is lessened by the addition of solvent. For example, we might say that a glass of iced tea becomes increasingly diluted as the ice melts. The water from the melting ice increases the volume of the solvent (water) and the overall volume of the solution (iced tea), thereby reducing the relative concentrations of the solutes that give the beverage its taste ([link](#)).



Both solutions contain the same mass of copper nitrate. The solution on the right is more dilute because the copper nitrate is dissolved in more solvent.
(credit: Mark Ott)

Dilution is also a common means of preparing solutions of a desired concentration. By adding solvent to a measured portion of a more concentrated *stock solution*, we can achieve a particular concentration. For example, commercial pesticides are typically sold as solutions in which the active ingredients are far more concentrated than is appropriate for their application. Before they can be used on crops, the pesticides must be diluted. This is also a very common practice for the preparation of a number of common laboratory reagents ([link](#)).



A solution of KMnO_4 is prepared by mixing water with 4.74 g of KMnO_4 in a flask.
(credit: modification of work by Mark Ott)

A simple mathematical relationship can be used to relate the volumes and concentrations of a solution before and after the dilution process. According to the definition of molarity, the molar amount of solute in a solution is equal to the product of the solution's molarity and its volume in liters:

Equation:

$$n = ML$$

Expressions like these may be written for a solution before and after it is diluted:

Equation:

$$n_1 = M_1L_1$$

Equation:

$$n_2 = M_2L_2$$

where the subscripts "1" and "2" refer to the solution before and after the dilution, respectively. Since the dilution process *does not change the amount of solute in the solution*, $n_1 = n_2$. Thus, these two equations may be set equal to one another:

Equation:

$$M_1L_1 = M_2L_2$$

This relation is commonly referred to as the dilution equation. Although we derived this equation using molarity as the unit of concentration and liters as the unit of volume, other units of concentration and volume may be used, so long as the units properly cancel per the factor-label method. Reflecting this versatility, the dilution equation is often written in the more general form:

Equation:

$$C_1V_1 = C_2V_2$$

where C and V are concentration and volume, respectively.

Note:



Use the [simulation](#) to explore the relations between solute amount, solution volume, and concentration and to confirm the dilution equation.

Example:

Determining the Concentration of a Diluted Solution

If 0.850 L of a 5.00- M solution of copper nitrate, $\text{Cu}(\text{NO}_3)_2$, is diluted to a volume of 1.80 L by the addition of water, what is the molarity of the diluted solution?

Solution

We are given the volume and concentration of a stock solution, V_1 and C_1 , and the volume of the resultant diluted solution, V_2 . We need to find the concentration of the diluted solution, C_2 . We thus rearrange the dilution equation in order to isolate C_2 :

Equation:

$$C_1V_1 = C_2V_2$$

$$C_2 = \frac{C_1V_1}{V_2}$$

Since the stock solution is being diluted by more than two-fold (volume is increased from 0.85 L to 1.80 L), we would expect the diluted solution's concentration to be less

than one-half 5 *M*. We will compare this ballpark estimate to the calculated result to check for any gross errors in computation (for example, such as an improper substitution of the given quantities). Substituting the given values for the terms on the right side of this equation yields:

Equation:

$$C_2 = \frac{0.850 \text{ L} \times 5.00 \frac{\text{mol}}{\text{L}}}{1.80 \text{ L}} = 2.36 \text{ M}$$

This result compares well to our ballpark estimate (it's a bit less than one-half the stock concentration, 5 *M*).

Check Your Learning

What is the concentration of the solution that results from diluting 25.0 mL of a 2.04-*M* solution of CH₃OH to 500.0 mL?

Note:

Answer:

0.102 *M* CH₃OH

Example:

Volume of a Diluted Solution

What volume of 0.12 *M* HBr can be prepared from 11 mL (0.011 L) of 0.45 *M* HBr?

Solution

We are given the volume and concentration of a stock solution, *V*₁ and *C*₁, and the concentration of the resultant diluted solution, *C*₂. We need to find the volume of the diluted solution, *V*₂. We thus rearrange the dilution equation in order to isolate *V*₂:

Equation:

$$C_1V_1 = C_2V_2$$

$$V_2 = \frac{C_1V_1}{C_2}$$

Since the diluted concentration (0.12 *M*) is slightly more than one-fourth the original concentration (0.45 *M*), we would expect the volume of the diluted solution to be roughly four times the original volume, or around 44 mL. Substituting the given values and solving for the unknown volume yields:

Equation:

$$V_2 = \frac{(0.45\text{ M})(0.011\text{ L})}{(0.12\text{ M})}$$
$$V_2 = 0.041\text{ L}$$

The volume of the 0.12-*M* solution is 0.041 L (41 mL). The result is reasonable and compares well with our rough estimate.

Check Your Learning

A laboratory experiment calls for 0.125 *M* HNO₃. What volume of 0.125 *M* HNO₃ can be prepared from 0.250 L of 1.88 *M* HNO₃?

Note:**Answer:**

3.76 L

Example:**Volume of a Concentrated Solution Needed for Dilution**

What volume of 1.59 *M* KOH is required to prepare 5.00 L of 0.100 *M* KOH?

Solution

We are given the concentration of a stock solution, *C*₁, and the volume and concentration of the resultant diluted solution, *V*₂ and *C*₂. We need to find the volume of the stock solution, *V*₁. We thus rearrange the dilution equation in order to isolate *V*₁:

Equation:

$$C_1V_1 = C_2V_2$$

$$V_1 = \frac{C_2V_2}{C_1}$$

Since the concentration of the diluted solution 0.100 *M* is roughly one-sixteenth that of the stock solution (1.59 *M*), we would expect the volume of the stock solution to be about one-sixteenth that of the diluted solution, or around 0.3 liters. Substituting the given values and solving for the unknown volume yields:

Equation:

$$V_1 = \frac{(0.100\text{ M})(5.00\text{ L})}{1.59\text{ M}}$$
$$V_1 = 0.314\text{ L}$$

Thus, we would need 0.314 L of the 1.59-*M* solution to prepare the desired solution. This result is consistent with our rough estimate.

Check Your Learning

What volume of a 0.575-*M* solution of glucose, C₆H₁₂O₆, can be prepared from 50.00 mL of a 3.00-*M* glucose solution?

Note:**Answer:**

0.261 L

Key Concepts and Summary

Solutions are homogeneous mixtures. Many solutions contain one component, called the solvent, in which other components, called solutes, are dissolved. An aqueous solution is one for which the solvent is water. The concentration of a solution is a measure of the relative amount of solute in a given amount of solution. Concentrations may be measured using various units, with one very useful unit being molarity, defined as the number of moles of solute per liter of solution. The solute concentration of a solution may be decreased by adding solvent, a process referred to as dilution. The dilution equation is a simple relation between concentrations and volumes of a solution before and after dilution.

Chemistry End of Chapter Exercises

Exercise:**Problem:**

Explain what changes and what stays the same when 1.00 L of a solution of NaCl is diluted to 1.80 L.

Exercise:

Problem:

What information do we need to calculate the molarity of a sulfuric acid solution?

Solution:

We need to know the number of moles of sulfuric acid dissolved in the solution and the volume of the solution.

Exercise:**Problem:**

What does it mean when we say that a 200-mL sample and a 400-mL sample of a solution of salt have the same molarity? In what ways are the two samples identical? In what ways are these two samples different?

Exercise:

Problem: Determine the molarity for each of the following solutions:

- (a) 0.444 mol of CoCl_2 in 0.654 L of solution
 - (b) 98.0 g of phosphoric acid, H_3PO_4 , in 1.00 L of solution
 - (c) 0.2074 g of calcium hydroxide, $\text{Ca}(\text{OH})_2$, in 40.00 mL of solution
 - (d) 10.5 kg of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in 18.60 L of solution
 - (e) 7.0×10^{-3} mol of I_2 in 100.0 mL of solution
 - (f) 1.8×10^4 mg of HCl in 0.075 L of solution
-

Solution:

- (a) 0.679 M;
- (b) 1.00 M;
- (c) 0.06998 M;
- (d) 1.75 M;
- (e) 0.070 M;
- (f) 6.6 M

Exercise:

Problem: Determine the molarity of each of the following solutions:

- (a) 1.457 mol KCl in 1.500 L of solution
- (b) 0.515 g of H_2SO_4 in 1.00 L of solution
- (c) 20.54 g of $\text{Al}(\text{NO}_3)_3$ in 1575 mL of solution
- (d) 2.76 kg of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 1.45 L of solution
- (e) 0.005653 mol of Br_2 in 10.00 mL of solution
- (f) 0.000889 g of glycine, $\text{C}_2\text{H}_5\text{NO}_2$, in 1.05 mL of solution

Exercise:

Problem:

Consider this question: What is the mass of the solute in 0.500 L of 0.30 *M* glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, used for intravenous injection?

- (a) Outline the steps necessary to answer the question.
 - (b) Answer the question.
-

Solution:

(a) determine the number of moles of glucose in 0.500 L of solution; determine the molar mass of glucose; determine the mass of glucose from the number of moles and its molar mass; (b) 27 g

Exercise:

Problem:

Consider this question: What is the mass of solute in 200.0 L of a 1.556-*M* solution of KBr?

- (a) Outline the steps necessary to answer the question.
- (b) Answer the question.

Exercise:

Problem:

Calculate the number of moles and the mass of the solute in each of the following solutions:

- (a) 2.00 L of 18.5 *M* H_2SO_4 , concentrated sulfuric acid

(b) 100.0 mL of $3.8 \times 10^{-5} \text{ M}$ NaCN, the minimum lethal concentration of sodium cyanide in blood serum

(c) 5.50 L of 13.3 M H_2CO , the formaldehyde used to “fix” tissue samples

(d) 325 mL of $1.8 \times 10^{-6} \text{ M}$ FeSO_4 , the minimum concentration of iron sulfate detectable by taste in drinking water

Solution:

(a) 37.0 mol H_2SO_4 ;

$3.63 \times 10^3 \text{ g}$ H_2SO_4 ;

(b) $3.8 \times 10^{-6} \text{ mol}$ NaCN;

$1.9 \times 10^{-4} \text{ g}$ NaCN;

(c) 73.2 mol H_2CO ;

2.20 kg H_2CO ;

(d) $5.9 \times 10^{-7} \text{ mol}$ FeSO_4 ;

$8.9 \times 10^{-5} \text{ g}$ FeSO_4

Exercise:

Problem:

Calculate the number of moles and the mass of the solute in each of the following solutions:

(a) 325 mL of $8.23 \times 10^{-5} \text{ M}$ KI, a source of iodine in the diet

(b) 75.0 mL of $2.2 \times 10^{-5} \text{ M}$ H_2SO_4 , a sample of acid rain

(c) 0.2500 L of 0.1135 M K_2CrO_4 , an analytical reagent used in iron assays

(d) 10.5 L of 3.716 M $(\text{NH}_4)_2\text{SO}_4$, a liquid fertilizer

Exercise:

Problem:

Consider this question: What is the molarity of KMnO_4 in a solution of 0.0908 g of KMnO_4 in 0.500 L of solution?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

Solution:

(a) Determine the molar mass of KMnO_4 ; determine the number of moles of KMnO_4 in the solution; from the number of moles and the volume of solution, determine the molarity; (b) $1.15 \times 10^{-3} \text{ M}$

Exercise:

Problem:

Consider this question: What is the molarity of HCl if 35.23 mL of a solution of HCl contain 0.3366 g of HCl?

- (a) Outline the steps necessary to answer the question.
- (b) Answer the question.

Exercise:

Problem: Calculate the molarity of each of the following solutions:

- (a) 0.195 g of cholesterol, $\text{C}_{27}\text{H}_{46}\text{O}$, in 0.100 L of serum, the average concentration of cholesterol in human serum
- (b) 4.25 g of NH_3 in 0.500 L of solution, the concentration of NH_3 in household ammonia
- (c) 1.49 kg of isopropyl alcohol, $\text{C}_3\text{H}_7\text{OH}$, in 2.50 L of solution, the concentration of isopropyl alcohol in rubbing alcohol
- (d) 0.029 g of I_2 in 0.100 L of solution, the solubility of I_2 in water at 20°C

Solution:

- (a) $5.04 \times 10^{-3} \text{ M}$;
- (b) 0.499 M ;
- (c) 9.92 M ;
- (d) $1.1 \times 10^{-3} \text{ M}$

Exercise:

Problem: Calculate the molarity of each of the following solutions:

- (a) 293 g HCl in 666 mL of solution, a concentrated HCl solution
- (b) 2.026 g FeCl_3 in 0.1250 L of a solution used as an unknown in general chemistry laboratories

(c) 0.001 mg Cd^{2+} in 0.100 L, the maximum permissible concentration of cadmium in drinking water

(d) 0.0079 g $\text{C}_7\text{H}_5\text{SNO}_3$ in one ounce (29.6 mL), the concentration of saccharin in a diet soft drink.

Exercise:

Problem:

There is about 1.0 g of calcium, as Ca^{2+} , in 1.0 L of milk. What is the molarity of Ca^{2+} in milk?

Solution:

0.025 M

Exercise:

Problem:

What volume of a 1.00-M $\text{Fe}(\text{NO}_3)_3$ solution can be diluted to prepare 1.00 L of a solution with a concentration of 0.250 M?

Exercise:

Problem:

If 0.1718 L of a 0.3556-M $\text{C}_3\text{H}_7\text{OH}$ solution is diluted to a concentration of 0.1222 M, what is the volume of the resulting solution?

Solution:

0.5000 L

Exercise:

Problem:

If 4.12 L of a 0.850 M- H_3PO_4 solution is be diluted to a volume of 10.00 L, what is the concentration of the resulting solution?

Exercise:

Problem:

What volume of a 0.33-M $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ solution can be diluted to prepare 25 mL of a solution with a concentration of 0.025 M?

Solution:

1.9 mL

Exercise:

Problem:

What is the concentration of the NaCl solution that results when 0.150 L of a 0.556-*M* solution is allowed to evaporate until the volume is reduced to 0.105 L?

Exercise:

Problem:

What is the molarity of the diluted solution when each of the following solutions is diluted to the given final volume?

(a) 1.00 L of a 0.250-*M* solution of $\text{Fe}(\text{NO}_3)_3$ is diluted to a final volume of 2.00 L

(b) 0.5000 L of a 0.1222-*M* solution of $\text{C}_3\text{H}_7\text{OH}$ is diluted to a final volume of 1.250 L

(c) 2.35 L of a 0.350-*M* solution of H_3PO_4 is diluted to a final volume of 4.00 L

(d) 22.50 mL of a 0.025-*M* solution of $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ is diluted to 100.0 mL

Solution:

(a) 0.125 *M*;

(b) 0.04888 *M*;

(c) 0.206 *M*;

(e) 0.0056 *M*

Exercise:

Problem:

What is the final concentration of the solution produced when 225.5 mL of a 0.09988-*M* solution of Na_2CO_3 is allowed to evaporate until the solution volume is reduced to 45.00 mL?

Exercise:

Problem:

A 2.00-L bottle of a solution of concentrated HCl was purchased for the general chemistry laboratory. The solution contained 868.8 g of HCl. What is the molarity of the solution?

Solution:

11.9 M

Exercise:

Problem:

An experiment in a general chemistry laboratory calls for a 2.00-M solution of HCl. How many mL of 11.9 M HCl would be required to make 250 mL of 2.00 M HCl?

Exercise:

Problem: What volume of a 0.20-M K_2SO_4 solution contains 57 g of K_2SO_4 ?

Solution:

1.6 L

Exercise:

Problem:

The US Environmental Protection Agency (EPA) places limits on the quantities of toxic substances that may be discharged into the sewer system. Limits have been established for a variety of substances, including hexavalent chromium, which is limited to 0.50 mg/L. If an industry is discharging hexavalent chromium as potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), what is the maximum permissible molarity of that substance?

Key Equations

- $M = \frac{\text{mol solute}}{\text{L solution}}$
- $C_1V_1 = C_2V_2$

Glossary

aqueous solution

solution for which water is the solvent

concentrated

qualitative term for a solution containing solute at a relatively high concentration

concentration

quantitative measure of the relative amounts of solute and solvent present in a solution

dilute

qualitative term for a solution containing solute at a relatively low concentration

dilution

process of adding solvent to a solution in order to lower the concentration of solutes

dissolved

describes the process by which solute components are dispersed in a solvent

molarity (M)

unit of concentration, defined as the number of moles of solute dissolved in 1 liter of solution

solute

solution component present in a concentration less than that of the solvent

solvent

solution component present in a concentration that is higher relative to other components

Chemical Reaction Rates

By the end of this section, you will be able to:

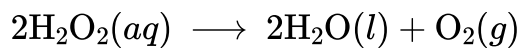
- Define chemical reaction rate
- Derive rate expressions from the balanced equation for a given chemical reaction
- Calculate reaction rates from experimental data

A *rate* is a measure of how some property varies with time. Speed is a familiar rate that expresses the distance traveled by an object in a given amount of time. Wage is a rate that represents the amount of money earned by a person working for a given amount of time. Likewise, the rate of a chemical reaction is a measure of how much reactant is consumed, or how much product is produced, by the reaction in a given amount of time.

The **rate of reaction** is the change in the amount of a reactant or product per unit time. Reaction rates are therefore determined by measuring the time dependence of some property that can be related to reactant or product amounts. Rates of reactions that consume or produce gaseous substances, for example, are conveniently determined by measuring changes in volume or pressure. For reactions involving one or more colored substances, rates may be monitored via measurements of light absorption. For reactions involving aqueous electrolytes, rates may be measured via changes in a solution's conductivity.

For reactants and products in solution, their relative amounts (concentrations) are conveniently used for purposes of expressing reaction rates. If we measure the concentration of hydrogen peroxide, H_2O_2 , in an aqueous solution, we find that it changes slowly over time as the H_2O_2 decomposes, according to the equation:

Equation:



The rate at which the hydrogen peroxide decomposes can be expressed in terms of the rate of change of its concentration, as shown here:

Equation:

$$\begin{aligned}\text{rate of decomposition of } \text{H}_2\text{O}_2 &= - \frac{\text{change in concentration of reactant}}{\text{time interval}} \\ &= - \frac{[\text{H}_2\text{O}_2]_{t_2} - [\text{H}_2\text{O}_2]_{t_1}}{t_2 - t_1} \\ &= - \frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t}\end{aligned}$$

This mathematical representation of the change in species concentration over time is the **rate expression** for the reaction. The brackets indicate molar concentrations, and the

symbol delta (Δ) indicates “change in.” Thus, $[\text{H}_2\text{O}_2]_{t_1}$ represents the molar concentration of hydrogen peroxide at some time t_1 ; likewise, $[\text{H}_2\text{O}_2]_{t_2}$ represents the molar concentration of hydrogen peroxide at a later time t_2 ; and $\Delta[\text{H}_2\text{O}_2]$ represents the change in molar concentration of hydrogen peroxide during the time interval Δt (that is, $t_2 - t_1$). Since the reactant concentration decreases as the reaction proceeds, $\Delta[\text{H}_2\text{O}_2]$ is a negative quantity; we place a negative sign in front of the expression because reaction rates are, by convention, positive quantities. [\[link\]](#) provides an example of data collected during the decomposition of H_2O_2 .

Time (h)	$[\text{H}_2\text{O}_2]$ (mol L ⁻¹)	$\Delta[\text{H}_2\text{O}_2]$ (mol L ⁻¹)	Δt (h)	Rate of Decomposition, (mol/L/h)
0.00	1.000	-0.500	6.00	0.0833
6.00	0.500			
12.00	0.250	-0.250	6.00	0.0417
18.00	0.125			
24.00	0.0625	-0.062	6.00	0.0103

The rate of decomposition of H_2O_2 in an aqueous solution decreases as the concentration of H_2O_2 decreases.

To obtain the tabulated results for this decomposition, the concentration of hydrogen peroxide was measured every 6 hours over the course of a day at a constant temperature of 40 °C. Reaction rates were computed for each time interval by dividing the change in concentration by the corresponding time increment, as shown here for the first 6-hour period:

Equation:

$$\frac{-\Delta[\text{H}_2\text{O}_2]}{\Delta t} = \frac{-(0.500 \text{ mol/L} - 1.000 \text{ mol/L})}{(6.00 \text{ h} - 0.00 \text{ h})} = 0.0833 \text{ mol L}^{-1} \text{ h}^{-1}$$

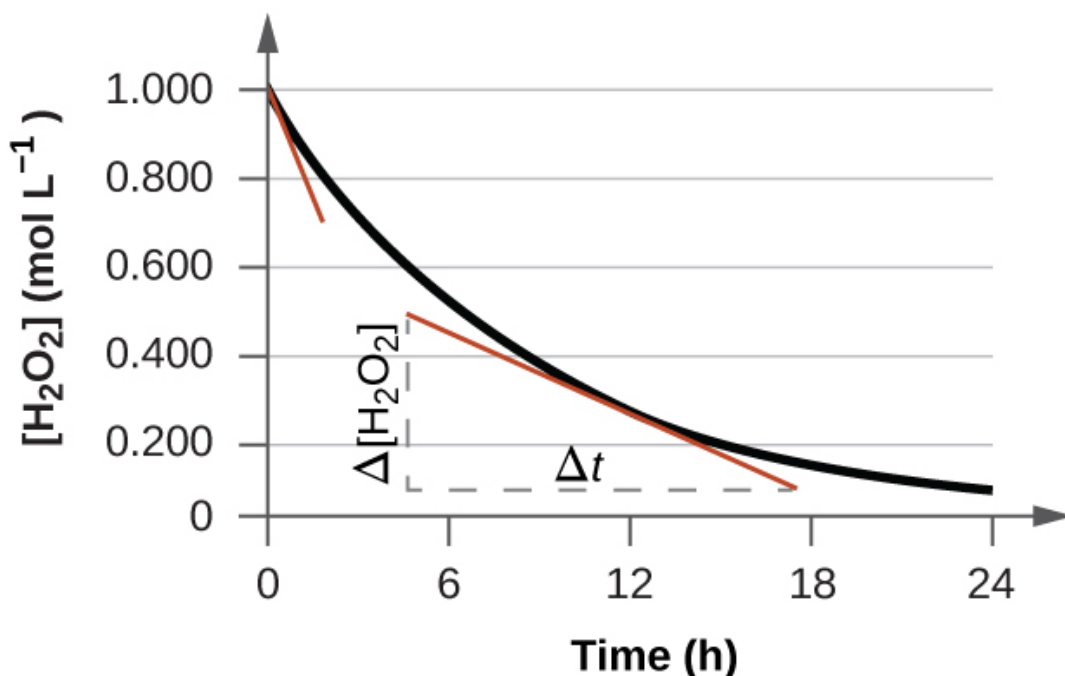
Notice that the reaction rates vary with time, decreasing as the reaction proceeds. Results for the last 6-hour period yield a reaction rate of:

Equation:

$$\frac{-\Delta[\text{H}_2\text{O}_2]}{\Delta t} = \frac{-(0.0625 \text{ mol/L} - 0.125 \text{ mol/L})}{(24.00 \text{ h} - 18.00 \text{ h})} = 0.0104 \text{ mol L}^{-1} \text{ h}^{-1}$$

This behavior indicates the reaction continually slows with time. Using the concentrations at the beginning and end of a time period over which the reaction rate is changing results in the calculation of an **average rate** for the reaction over this time interval. At any specific time, the rate at which a reaction is proceeding is known as its **instantaneous rate**. The instantaneous rate of a reaction at “time zero,” when the reaction commences, is its **initial rate**. Consider the analogy of a car slowing down as it approaches a stop sign. The vehicle’s initial rate—analogue to the beginning of a chemical reaction—would be the speedometer reading at the moment the driver begins pressing the brakes (t_0). A few moments later, the instantaneous rate at a specific moment—call it t_1 —would be somewhat slower, as indicated by the speedometer reading at that point in time. As time passes, the instantaneous rate will continue to fall until it reaches zero, when the car (or reaction) stops. Unlike instantaneous speed, the car’s average speed is not indicated by the speedometer; but it can be calculated as the ratio of the distance traveled to the time required to bring the vehicle to a complete stop (Δt). Like the decelerating car, the average rate of a chemical reaction will fall somewhere between its initial and final rates.

The instantaneous rate of a reaction may be determined one of two ways. If experimental conditions permit the measurement of concentration changes over very short time intervals, then average rates computed as described earlier provide reasonably good approximations of instantaneous rates. Alternatively, a graphical procedure may be used that, in effect, yields the results that would be obtained if short time interval measurements were possible. If we plot the concentration of hydrogen peroxide against time, the instantaneous rate of decomposition of H_2O_2 at any time t is given by the slope of a straight line that is tangent to the curve at that time ([link](#)). We can use calculus to evaluating the slopes of such tangent lines, but the procedure for doing so is beyond the scope of this chapter.



This graph shows a plot of concentration versus time for a 1.000 M solution of H_2O_2 . The rate at any instant is equal to the opposite of the slope of a line tangential to this curve at that time. Tangents are shown at $t = 0$ h (“initial rate”) and at $t = 10$ h (“instantaneous rate” at that particular time).

Note:

Reaction Rates in Analysis: Test Strips for Urinalysis

Physicians often use disposable test strips to measure the amounts of various substances in a patient’s urine ([\[link\]](#)). These test strips contain various chemical reagents, embedded in small pads at various locations along the strip, which undergo changes in color upon exposure to sufficient concentrations of specific substances. The usage instructions for test strips often stress that proper read time is critical for optimal results. This emphasis on read time suggests that kinetic aspects of the chemical reactions occurring on the test strip are important considerations.

The test for urinary glucose relies on a two-step process represented by the chemical equations shown here:

Equation:

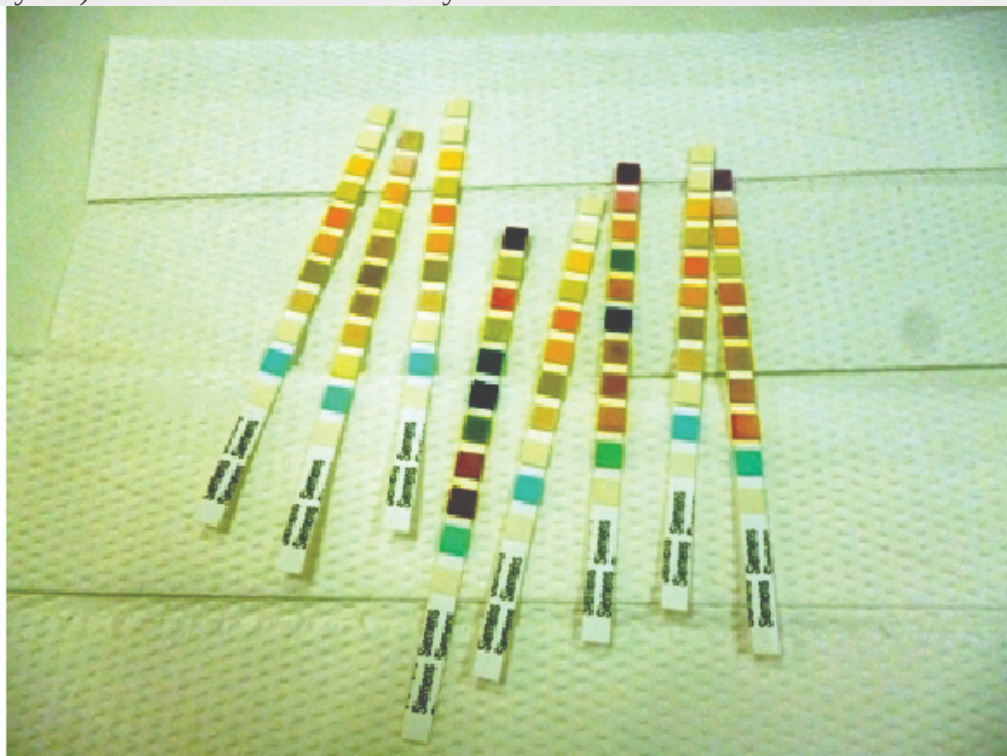


Equation:



The first equation depicts the oxidation of glucose in the urine to yield glucolactone and hydrogen peroxide. The hydrogen peroxide produced subsequently oxidizes colorless iodide ion to yield brown iodine, which may be visually detected. Some strips include an additional substance that reacts with iodine to produce a more distinct color change.

The two test reactions shown above are inherently very slow, but their rates are increased by special enzymes embedded in the test strip pad. This is an example of *catalysis*, a topic discussed later in this chapter. A typical glucose test strip for use with urine requires approximately 30 seconds for completion of the color-forming reactions. Reading the result too soon might lead one to conclude that the glucose concentration of the urine sample is lower than it actually is (a *false-negative* result). Waiting too long to assess the color change can lead to a *false positive* due to the slower (not catalyzed) oxidation of iodide ion by other substances found in urine.



Test strips are commonly used to detect the presence of specific substances in a person's urine. Many test strips have several pads containing various reagents to permit the detection of multiple substances on a single strip.

(credit: Iqbal Osman)

Relative Rates of Reaction

The rate of a reaction may be expressed in terms of the change in the amount of any reactant or product, and may be simply derived from the stoichiometry of the reaction. Consider the reaction represented by the following equation:

Equation:



The stoichiometric factors derived from this equation may be used to relate reaction rates in the same manner that they are used to relate reactant and product amounts. The relation between the reaction rates expressed in terms of nitrogen production and ammonia consumption, for example, is:

Equation:

$$-\frac{\Delta \text{mol NH}_3}{\Delta t} \times \frac{1 \text{ mol N}_2}{2 \text{ mol NH}_3} = \frac{\Delta \text{mol N}_2}{\Delta t}$$

We can express this more simply without showing the stoichiometric factor's units:

Equation:

$$-\frac{1}{2} \frac{\Delta \text{mol NH}_3}{\Delta t} = \frac{\Delta \text{mol N}_2}{\Delta t}$$

Note that a negative sign has been added to account for the opposite signs of the two amount changes (the reactant amount is decreasing while the product amount is increasing). If the reactants and products are present in the same solution, the molar amounts may be replaced by concentrations:

Equation:

$$-\frac{1}{2} \frac{\Delta [\text{NH}_3]}{\Delta t} = \frac{\Delta [\text{N}_2]}{\Delta t}$$

Similarly, the rate of formation of H_2 is three times the rate of formation of N_2 because three moles of H_2 form during the time required for the formation of one mole of N_2 :

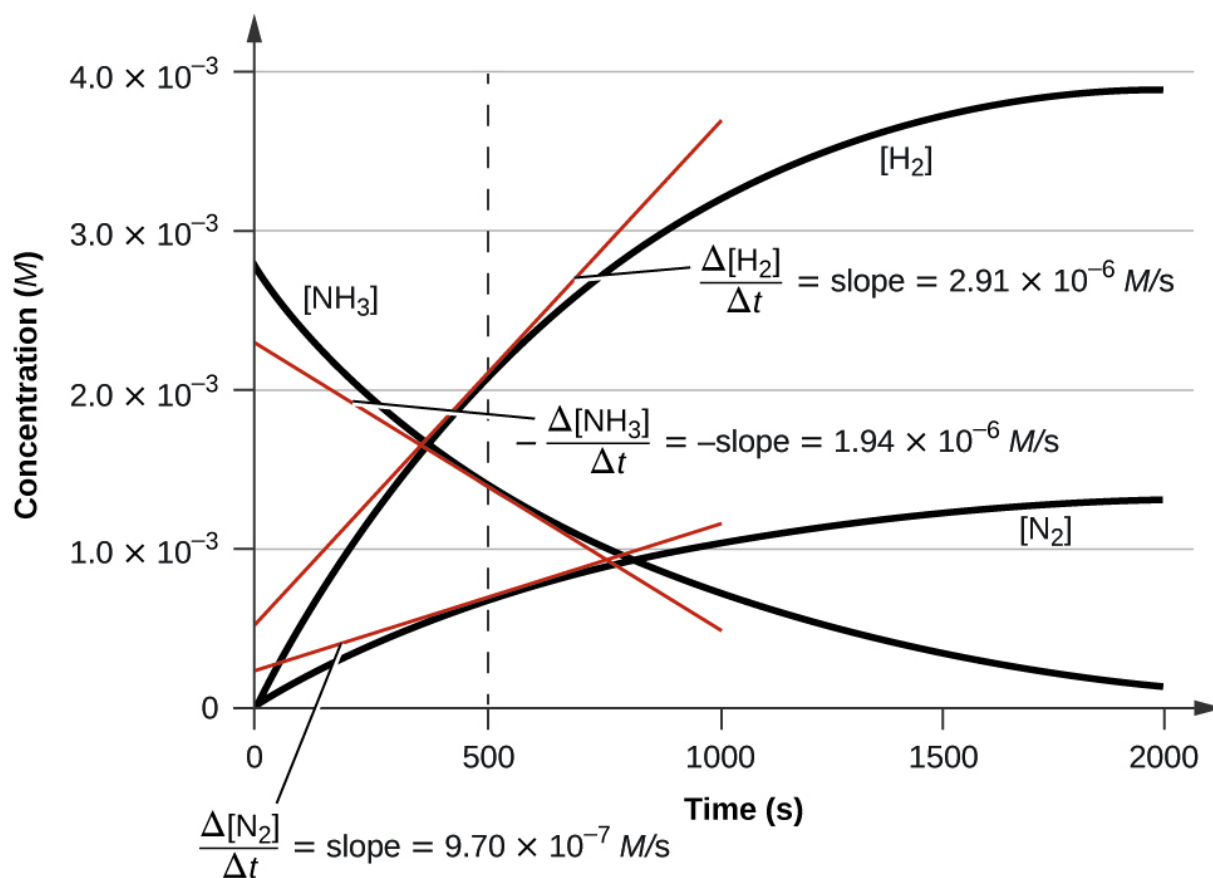
Equation:

$$\frac{1}{3} \frac{\Delta [\text{H}_2]}{\Delta t} = \frac{\Delta [\text{N}_2]}{\Delta t}$$

[\[link\]](#) illustrates the change in concentrations over time for the decomposition of ammonia into nitrogen and hydrogen at 1100 °C. We can see from the slopes of the tangents drawn at $t = 500$ seconds that the instantaneous rates of change in the concentrations of the reactants and products are related by their stoichiometric factors. The rate of hydrogen production, for example, is observed to be three times greater than that for nitrogen production:

Equation:

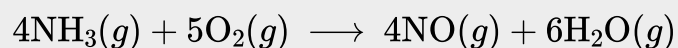
$$\frac{2.91 \times 10^{-6} \text{ M/s}}{9.70 \times 10^{-7} \text{ M/s}} \approx 3$$



This graph shows the changes in concentrations of the reactants and products during the reaction $2\text{NH}_3 \longrightarrow \text{N}_2 + 3\text{H}_2$. The rates of change of the three concentrations are related by their stoichiometric factors, as shown by the different slopes of the tangents at $t = 500$ s.

Example:**Expressions for Relative Reaction Rates**

The first step in the production of nitric acid is the combustion of ammonia:

Equation:

Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

Solution

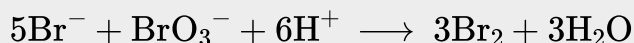
Considering the stoichiometry of this homogeneous reaction, the rates for the consumption of reactants and formation of products are:

Equation:

$$-\frac{1}{4} \frac{\Delta[\text{NH}_3]}{\Delta t} = -\frac{1}{5} \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{4} \frac{\Delta[\text{NO}]}{\Delta t} = \frac{1}{6} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

Check Your Learning

The rate of formation of Br_2 is $6.0 \times 10^{-6} \text{ mol/L/s}$ in a reaction described by the following net ionic equation:

Equation:

Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

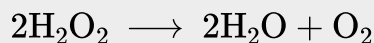
Note:**Answer:**

$$-\frac{1}{5} \frac{\Delta[\text{Br}^-]}{\Delta t} = -\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = -\frac{1}{6} \frac{\Delta[\text{H}^+]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{Br}_2]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

Example:**Reaction Rate Expressions for Decomposition of H_2O_2**

The graph in [\[link\]](#) shows the rate of the decomposition of H_2O_2 over time:

Equation:



Based on these data, the instantaneous rate of decomposition of H_2O_2 at $t = 11.1$ h is determined to be

$3.20 \times 10^{-2} \text{ mol/L/h}$, that is:

Equation:

$$-\frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t} = 3.20 \times 10^{-2} \text{ mol L}^{-1} \text{ h}^{-1}$$

What is the instantaneous rate of production of H_2O and O_2 ?

Solution

Using the stoichiometry of the reaction, we may determine that:

Equation:

$$-\frac{1}{2} \frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t} = \frac{\Delta[\text{O}_2]}{\Delta t}$$

Therefore:

Equation:

$$\frac{1}{2} \times 3.20 \times 10^{-2} \text{ mol L}^{-1} \text{ h}^{-1} = \frac{\Delta[\text{O}_2]}{\Delta t}$$

and

Equation:

$$\frac{\Delta[\text{O}_2]}{\Delta t} = 1.60 \times 10^{-2} \text{ mol L}^{-1} \text{ h}^{-1}$$

Check Your Learning

If the rate of decomposition of ammonia, NH_3 , at 1150 K is $2.10 \times 10^{-6} \text{ mol/L/s}$, what is the rate of production of nitrogen and hydrogen?

Note:

Answer:

$1.05 \times 10^{-6} \text{ mol/L/s}$, N_2 and $3.15 \times 10^{-6} \text{ mol/L/s}$, H_2 .

Key Concepts and Summary

The rate of a reaction can be expressed either in terms of the decrease in the amount of a reactant or the increase in the amount of a product per unit time. Relations between different rate expressions for a given reaction are derived directly from the stoichiometric coefficients of the equation representing the reaction.

Key Equations

- relative reaction rates for $aA \longrightarrow bB = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = \frac{1}{b} \frac{\Delta[B]}{\Delta t}$

Chemistry End of Chapter Exercises

Exercise:

Problem:

What is the difference between average rate, initial rate, and instantaneous rate?

Solution:

The instantaneous rate is the rate of a reaction at any particular point in time, a period of time that is so short that the concentrations of reactants and products change by a negligible amount. The initial rate is the instantaneous rate of reaction as it starts (as product just begins to form). Average rate is the average of the instantaneous rates over a time period.

Exercise:

Problem:

Ozone decomposes to oxygen according to the equation $2\text{O}_3(g) \longrightarrow 3\text{O}_2(g)$. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of O_3 and the formation of oxygen.

Exercise:

Problem:

In the nuclear industry, chlorine trifluoride is used to prepare uranium hexafluoride, a volatile compound of uranium used in the separation of uranium isotopes. Chlorine trifluoride is prepared by the reaction $\text{Cl}_2(g) + 3\text{F}_2(g) \longrightarrow 2\text{ClF}_3(g)$. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of Cl_2 and F_2 and the formation of ClF_3 .

Solution:

$$\text{rate} = +\frac{1}{2} \frac{\Delta[\text{ClF}_3]}{\Delta t} = -\frac{\Delta[\text{Cl}_2]}{\Delta t} = -\frac{1}{3} \frac{\Delta[\text{F}_2]}{\Delta t}$$

Exercise:**Problem:**

A study of the rate of dimerization of C_4H_6 gave the data shown in the table:



Time (s)	0	1600	3200	4800	6200
$[\text{C}_4\text{H}_6]$ (M)	1.00×10^{-2}	5.04×10^{-3}	3.37×10^{-3}	2.53×10^{-3}	2.08×10^{-3}

- (a) Determine the average rate of dimerization between 0 s and 1600 s, and between 1600 s and 3200 s.
- (b) Estimate the instantaneous rate of dimerization at 3200 s from a graph of time versus $[\text{C}_4\text{H}_6]$. What are the units of this rate?
- (c) Determine the average rate of formation of C_8H_{12} at 1600 s and the instantaneous rate of formation at 3200 s from the rates found in parts (a) and (b).

Exercise:**Problem:**

A study of the rate of the reaction represented as $2A \longrightarrow B$ gave the following data:

Time (s)	0.0	5.0	10.0	15.0	20.0	25.0	35.0
----------	-----	-----	------	------	------	------	------

[A] (M)	1.00	0.775	0.625	0.465	0.360	0.285	0.230
------------	------	-------	-------	-------	-------	-------	-------

(a) Determine the average rate of disappearance of A between 0.0 s and 10.0 s, and between 10.0 s and 20.0 s.

(b) Estimate the instantaneous rate of disappearance of A at 15.0 s from a graph of time versus [A]. What are the units of this rate?

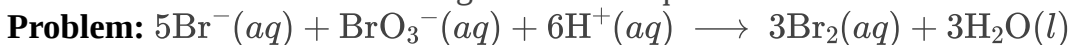
(c) Use the rates found in parts (a) and (b) to determine the average rate of formation of B between 0.00 s and 10.0 s, and the instantaneous rate of formation of B at 15.0 s.

Solution:

(a) average rate, 0 – 10 s = $0.0375 \text{ mol L}^{-1} \text{ s}^{-1}$; average rate, 10 – 20 s = $0.0265 \text{ mol L}^{-1} \text{ s}^{-1}$; (b) instantaneous rate, 15 s = $0.023 \text{ mol L}^{-1} \text{ s}^{-1}$; (c) average rate for B formation = $0.0188 \text{ mol L}^{-1} \text{ s}^{-1}$; instantaneous rate for B formation = $0.012 \text{ mol L}^{-1} \text{ s}^{-1}$

Exercise:

Consider the following reaction in aqueous solution:



If the rate of disappearance of $\text{Br}^-(aq)$ at a particular moment during the reaction is $3.5 \times 10^{-4} \text{ M s}^{-1}$, what is the rate of appearance of $\text{Br}_2(aq)$ at that moment?

Glossary

average rate

rate of a chemical reaction computed as the ratio of a measured change in amount or concentration of substance to the time interval over which the change occurred

initial rate

instantaneous rate of a chemical reaction at $t = 0$ s (immediately after the reaction has begun)

instantaneous rate

rate of a chemical reaction at any instant in time, determined by the slope of the line tangential to a graph of concentration as a function of time

rate of reaction

measure of the speed at which a chemical reaction takes place

rate expression

mathematical representation relating reaction rate to changes in amount, concentration, or pressure of reactant or product species per unit time

Factors Affecting Reaction Rates

By the end of this section, you will be able to:

- Describe the effects of chemical nature, physical state, temperature, concentration, and catalysis on reaction rates

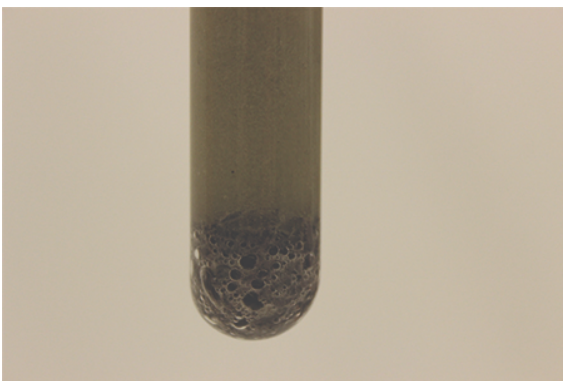
The rates at which reactants are consumed and products are formed during chemical reactions vary greatly. We can identify five factors that affect the rates of chemical reactions: the chemical nature of the reacting substances, the state of subdivision (one large lump versus many small particles) of the reactants, the temperature of the reactants, the concentration of the reactants, and the presence of a catalyst.

The Chemical Nature of the Reacting Substances

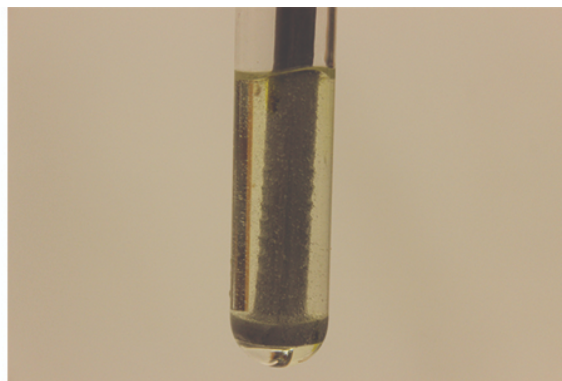
The rate of a reaction depends on the nature of the participating substances. Reactions that appear similar may have different rates under the same conditions, depending on the identity of the reactants. For example, when small pieces of the metals iron and sodium are exposed to air, the sodium reacts completely with air overnight, whereas the iron is barely affected. The active metals calcium and sodium both react with water to form hydrogen gas and a base. Yet calcium reacts at a moderate rate, whereas sodium reacts so rapidly that the reaction is almost explosive.

The State of Subdivision of the Reactants

Except for substances in the gaseous state or in solution, reactions occur at the boundary, or interface, between two phases. Hence, the rate of a reaction between two phases depends to a great extent on the surface contact between them. A finely divided solid has more surface area available for reaction than does one large piece of the same substance. Thus a liquid will react more rapidly with a finely divided solid than with a large piece of the same solid. For example, large pieces of iron react slowly with acids; finely divided iron reacts much more rapidly ([\[link\]](#)). Large pieces of wood smolder, smaller pieces burn rapidly, and saw dust burns explosively.



(a)



(b)

(a) Iron powder reacts rapidly with dilute hydrochloric acid and produces bubbles of hydrogen gas because the powder has a large total surface area: $2\text{Fe}(s) + 6\text{HCl}(aq) \longrightarrow 2\text{FeCl}_3(aq) + 3\text{H}_2(g)$. (b) An iron nail reacts more slowly.

Note:



Watch [this video](#) to see the reaction of cesium with water in slow motion and a discussion of how the state of reactants and particle size affect reaction rates.

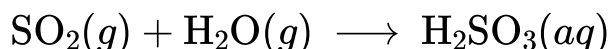
Temperature of the Reactants

Chemical reactions typically occur faster at higher temperatures. Food can spoil quickly when left on the kitchen counter. However, the lower temperature inside of a refrigerator slows that process so that the same food remains fresh for days. We use a burner or a hot plate in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures. In many cases, an increase in temperature of only 10 °C will approximately double the rate of a reaction in a homogeneous system.

Concentrations of the Reactants

The rates of many reactions depend on the concentrations of the reactants. Rates usually increase when the concentration of one or more of the reactants increases. For example, calcium carbonate (CaCO₃) deteriorates as a result of its reaction with the pollutant sulfur dioxide. The rate of this reaction depends on the amount of sulfur dioxide in the air ([link](#)). An acidic oxide, sulfur dioxide combines with water vapor in the air to produce sulfurous acid in the following reaction:

Equation:



Calcium carbonate reacts with sulfurous acid as follows:

Equation:



In a polluted atmosphere where the concentration of sulfur dioxide is high, calcium carbonate deteriorates more rapidly than in less polluted air. Similarly, phosphorus burns much more rapidly in an atmosphere of pure oxygen than in air, which is only about 20% oxygen.



Statues made from carbonate compounds such as limestone and marble typically weather slowly over time due to the actions of water, and thermal expansion and contraction. However, pollutants like sulfur dioxide can accelerate weathering. As the concentration of air pollutants increases, deterioration of limestone occurs more rapidly.
(credit: James P Fisher III)

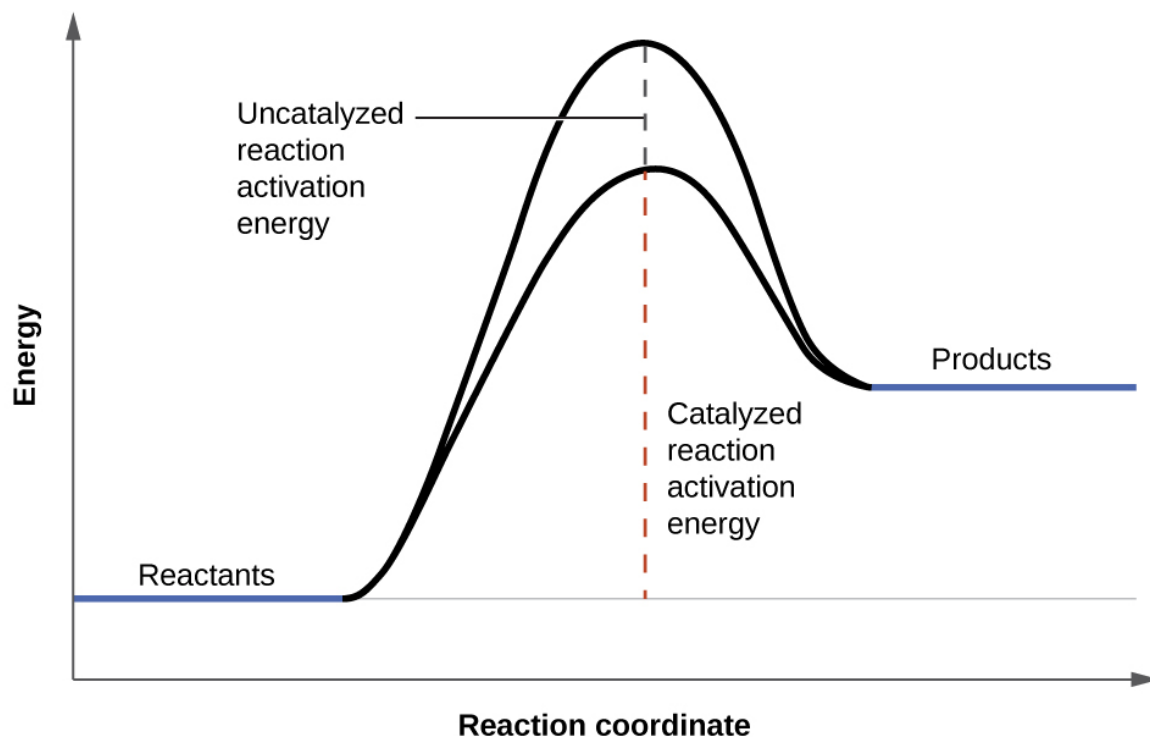
Note:



Phosphorous burns rapidly in air, but it will burn even more rapidly if the concentration of oxygen is higher. Watch this [video](#) to see an example.

The Presence of a Catalyst

Hydrogen peroxide solutions foam when poured onto an open wound because substances in the exposed tissues act as catalysts, increasing the rate of hydrogen peroxide's decomposition. However, in the absence of these catalysts (for example, in the bottle in the medicine cabinet) complete decomposition can take months. A **catalyst** is a substance that increases the rate of a chemical reaction by lowering the activation energy without itself being consumed by the reaction. Activation energy is the minimum amount of energy required for a chemical reaction to proceed in the forward direction. A catalyst increases the reaction rate by providing an alternative pathway or mechanism for the reaction to follow ([link](#)). Catalysis will be discussed in greater detail later in this chapter as it relates to mechanisms of reactions.



The presence of a catalyst increases the rate of a reaction by lowering its activation energy.

Note:



Chemical reactions occur when molecules collide with each other and undergo a chemical transformation. Before physically performing a reaction in a laboratory, scientists can use molecular modeling simulations

to predict how the parameters discussed earlier will influence the rate of a reaction. Use the [PhET Reactions & Rates interactive](#) to explore how temperature, concentration, and the nature of the reactants affect reaction rates.

Key Concepts and Summary

The rate of a chemical reaction is affected by several parameters. Reactions involving two phases proceed more rapidly when there is greater surface area contact. If temperature or reactant concentration is increased, the rate of a given reaction generally increases as well. A catalyst can increase the rate of a reaction by providing an alternative pathway that causes the activation energy of the reaction to decrease.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Describe the effect of each of the following on the rate of the reaction of magnesium metal with a solution of hydrochloric acid: the molarity of the hydrochloric acid, the temperature of the solution, and the size of the pieces of magnesium.

Solution:

Higher molarity increases the rate of the reaction. Higher temperature increases the rate of the reaction. Smaller pieces of magnesium metal will react more rapidly than larger pieces because more reactive surface exists.

Exercise:

Problem:

Explain why an egg cooks more slowly in boiling water in Denver than in New York City. (Hint: Consider the effect of temperature on reaction rate and the effect of pressure on boiling point.)

Exercise:**Problem:**

Go to the [PhET Reactions & Rates](#) interactive. Use the Single Collision tab to represent how the collision between monatomic oxygen (O) and carbon monoxide (CO) results in the breaking of one bond and the formation of another. Pull back on the red plunger to release the atom and observe the results. Then, click on “Reload Launcher” and change to “Angled shot” to see the difference.

(a) What happens when the angle of the collision is changed?

(b) Explain how this is relevant to rate of reaction.

Solution:

(a) Depending on the angle selected, the atom may take a long time to collide with the molecule and, when a collision does occur, it may not result in the breaking of the bond and the forming of the other. (b) Particles of reactant must come into contact with each other before they can react.

Exercise:**Problem:**

In the [PhET Reactions & Rates](#) interactive, use the “Many Collisions” tab to observe how multiple atoms and molecules interact under varying conditions. Select a molecule to pump into the chamber. Set the initial temperature and select the current amounts of each reactant. Select “Show bonds” under Options. How is the rate of the reaction affected by concentration and temperature?

Exercise:

Problem:

In the [PhET Reactions & Rates](#) interactive, on the Many Collisions tab, set up a simulation with 15 molecules of A and 10 molecules of BC. Select “Show Bonds” under Options.

(a) Leave the Initial Temperature at the default setting. Observe the reaction. Is the rate of reaction fast or slow?

(b) Click “Pause” and then “Reset All,” and then enter 15 molecules of A and 10 molecules of BC once again. Select “Show Bonds” under Options. This time, increase the initial temperature until, on the graph, the total average energy line is completely above the potential energy curve. Describe what happens to the reaction.

Solution:

(a) very slow; (b) As the temperature is increased, the reaction proceeds at a faster rate. The amount of reactants decreases, and the amount of products increases. After a while, there is a roughly equal amount of *BC*, *AB*, and *C* in the mixture and a slight excess of *A*.

Glossary

catalyst

substance that increases the rate of a reaction without itself being consumed by the reaction

Rate Laws

By the end of this section, you will be able to:

- Explain the form and function of a rate law
- Use rate laws to calculate reaction rates
- Use rate and concentration data to identify reaction orders and derive rate laws

As described in the previous module, the rate of a reaction is affected by the concentrations of reactants. **Rate laws** or **rate equations** are mathematical expressions that describe the relationship between the rate of a chemical reaction and the concentration of its reactants. In general, a rate law (or differential rate law, as it is sometimes called) takes this form:

Equation:

$$\text{rate} = k[A]^m[B]^n[C]^p \dots$$

in which $[A]$, $[B]$, and $[C]$ represent the molar concentrations of reactants, and k is the **rate constant**, which is specific for a particular reaction at a particular temperature. The exponents m , n , and p are usually positive integers (although it is possible for them to be fractions or negative numbers). The rate constant k and the exponents m , n , and p must be determined experimentally by observing how the rate of a reaction changes as the concentrations of the reactants are changed. The rate constant k is independent of the concentration of A , B , or C , but it does vary with temperature and surface area.

The exponents in a rate law describe the effects of the reactant concentrations on the reaction rate and define the **reaction order**. Consider a reaction for which the rate law is:

Equation:

$$\text{rate} = k[A]^m[B]^n$$

If the exponent m is 1, the reaction is first order with respect to A . If m is 2, the reaction is second order with respect to A . If n is 1, the reaction is first order in B . If n is 2, the reaction is second order in B . If m or n is zero, the reaction is zero order in A or B , respectively, and the rate of the reaction is not affected by the concentration of that reactant. The **overall reaction order** is the sum of the orders with respect to each reactant. If $m = 1$ and $n = 1$, the overall order of the reaction is second order ($m + n = 1 + 1 = 2$).

The rate law:

Equation:

$$\text{rate} = k[\text{H}_2\text{O}_2]$$

describes a reaction that is first order in hydrogen peroxide and first order overall. The rate law:

Equation:

$$\text{rate} = k[\text{C}_4\text{H}_6]^2$$

describes a reaction that is second order in C_4H_6 and second order overall. The rate law:

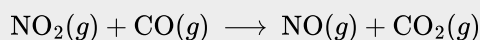
Equation:

$$\text{rate} = k[\text{H}^+][\text{OH}^-]$$

describes a reaction that is first order in H^+ , first order in OH^- , and second order overall.

Example:**Writing Rate Laws from Reaction Orders**

An experiment shows that the reaction of nitrogen dioxide with carbon monoxide:

Equation:

is second order in NO_2 and zero order in CO at 100°C . What is the rate law for the reaction?

Solution

The reaction will have the form:

Equation:

$$\text{rate} = k[\text{NO}_2]^m[\text{CO}]^n$$

The reaction is second order in NO_2 ; thus $m = 2$. The reaction is zero order in CO ; thus $n = 0$. The rate law is:

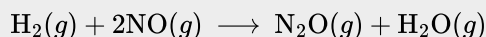
Equation:

$$\text{rate} = k[\text{NO}_2]^2[\text{CO}]^0 = k[\text{NO}_2]^2$$

Remember that a number raised to the zero power is equal to 1, thus $[\text{CO}]^0 = 1$, which is why we can simply drop the concentration of CO from the rate equation: the rate of reaction is solely dependent on the concentration of NO_2 . When we consider rate mechanisms later in this chapter, we will explain how a reactant's concentration can have no effect on a reaction despite being involved in the reaction.

Check Your Learning

The rate law for the reaction:

Equation:

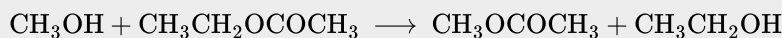
has been determined to be $\text{rate} = k[\text{NO}]^2[\text{H}_2]$. What are the orders with respect to each reactant, and what is the overall order of the reaction?

Note:**Answer:**

order in $\text{NO} = 2$; order in $\text{H}_2 = 1$; overall order = 3

Check Your Learning

In a transesterification reaction, a triglyceride reacts with an alcohol to form an ester and glycerol. Many students learn about the reaction between methanol (CH_3OH) and ethyl acetate ($\text{CH}_3\text{CH}_2\text{OCOCH}_3$) as a sample reaction before studying the chemical reactions that produce biodiesel:

Equation:

The rate law for the reaction between methanol and ethyl acetate is, under certain conditions, determined to be:

Equation:

$$\text{rate} = k[\text{CH}_3\text{OH}]$$

What is the order of reaction with respect to methanol and ethyl acetate, and what is the overall order of reaction?

Note:

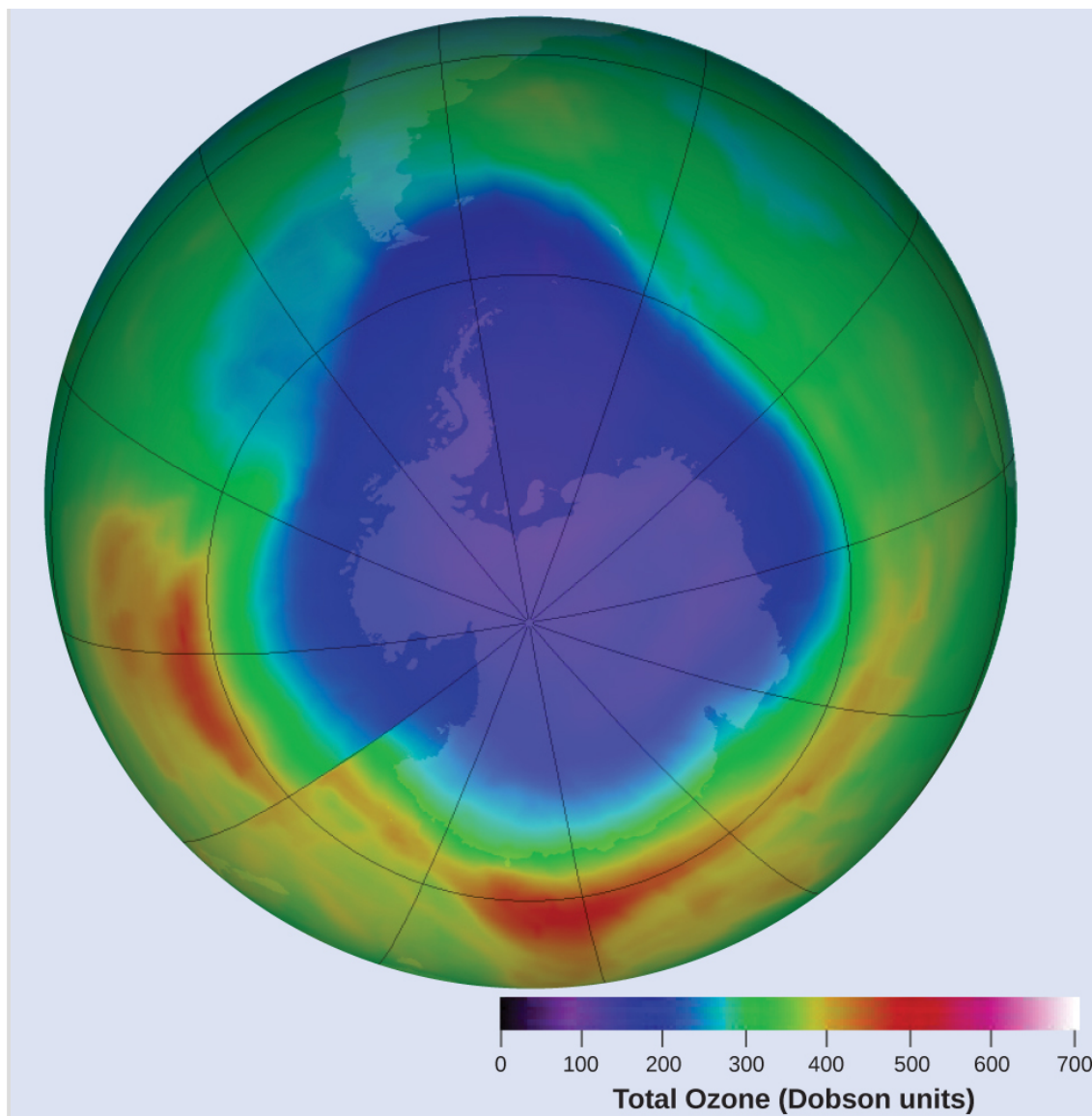
Answer:

order in $\text{CH}_3\text{OH} = 1$; order in $\text{CH}_3\text{CH}_2\text{OCOCH}_3 = 0$; overall order = 1

It is sometimes helpful to use a more explicit algebraic method, often referred to as the **method of initial rates**, to determine the orders in rate laws. To use this method, we select two sets of rate data that differ in the concentration of only one reactant and set up a ratio of the two rates and the two rate laws. After canceling terms that are equal, we are left with an equation that contains only one unknown, the coefficient of the concentration that varies. We then solve this equation for the coefficient.

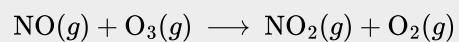
Example:**Determining a Rate Law from Initial Rates**

Ozone in the upper atmosphere is depleted when it reacts with nitrogen oxides. The rates of the reactions of nitrogen oxides with ozone are important factors in deciding how significant these reactions are in the formation of the ozone hole over Antarctica ([link](#)). One such reaction is the combination of nitric oxide, NO, with ozone, O_3 :



Over the past several years, the atmospheric ozone concentration over Antarctica has decreased during the winter. This map shows the decreased concentration as a purple area. (credit: modification of work by NASA)

Equation:



This reaction has been studied in the laboratory, and the following rate data were determined at 25 °C.

Trial	[NO] (mol/L)	[O ₃] (mol/L)	$\frac{\Delta[\text{NO}_2]}{\Delta t}$ (mol L ⁻¹ s ⁻¹)
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Trial	[NO] (mol/L)	[O ₃] (mol/L)	$\frac{\Delta[\text{NO}_2]}{\Delta t}$ (mol L ⁻¹ s ⁻¹)
1	1.00×10^{-6}	3.00×10^{-6}	6.60×10^{-5}
2	1.00×10^{-6}	6.00×10^{-6}	1.32×10^{-4}
3	1.00×10^{-6}	9.00×10^{-6}	1.98×10^{-4}
4	2.00×10^{-6}	9.00×10^{-6}	3.96×10^{-4}
5	3.00×10^{-6}	9.00×10^{-6}	5.94×10^{-4}

Determine the rate law and the rate constant for the reaction at 25 °C.

Solution

The rate law will have the form:

Equation:

$$\text{rate} = k[\text{NO}]^m[\text{O}_3]^n$$

We can determine the values of m , n , and k from the experimental data using the following three-part process:

Determine the value of m from the data in which [NO] varies and [O₃] is constant. In the last three experiments, [NO] varies while [O₃] remains constant. When [NO] doubles from trial 3 to 4, the rate doubles, and when [NO] triples from trial 3 to 5, the rate also triples. Thus, the rate is also directly proportional to [NO], and m in the rate law is equal to 1.

Equation:

Determine the value of n from data in which [O₃] varies and [NO] is constant. In the first three experiments, [NO] is constant and [O₃] varies. The rate = $k[\text{NO}]^1[\text{O}_3]^1 = k[\text{NO}][\text{O}_3]$ reaction rate changes in direct proportion to the change in [O₃]. When [O₃] doubles from trial 1 to 2, the rate doubles; when [O₃] triples from trial 1 to 3, the rate increases also triples. Thus, the rate is directly proportional to [O₃], and n is equal to 1. The rate law is thus:

Equation:

Determine the value of k from one set of concentrations and the corresponding rate.

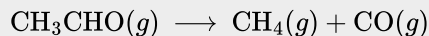
$$\begin{aligned}
 k &= \frac{\text{rate}}{[\text{NO}][\text{O}_3]} \\
 &= \frac{6.60 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}}{(1.00 \times 10^{-6} \text{ mol L}^{-1})(3.00 \times 10^{-6} \text{ mol L}^{-1})} \text{ enough.} \\
 &= 2.20 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}
 \end{aligned}$$

The large value of k tells us that this is a fast reaction that could play an important role in ozone depletion if [NO] is large enough.

Check Your Learning

Acetaldehyde decomposes when heated to yield methane and carbon monoxide according to the equation:

Equation:



Determine the rate law and the rate constant for the reaction from the following experimental data:

Trial	[CH ₃ CHO] (mol/L)	$-\frac{\Delta[\text{CH}_3\text{CHO}]}{\Delta t}$ (mol L ⁻¹ s ⁻¹)
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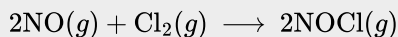
Trial	[CH ₃ CHO] (mol/L)	$-\frac{\Delta[\text{CH}_3\text{CHO}]}{\Delta t}$ (mol L ⁻¹ s ⁻¹)
1	1.75×10^{-3}	2.06×10^{-11}
2	3.50×10^{-3}	8.24×10^{-11}
3	7.00×10^{-3}	3.30×10^{-10}
Note: Answer: rate = $k[\text{CH}_3\text{CHO}]^2$ with $k = 6.73 \times 10^{-6}$ L/mol/s		

Example:

Determining Rate Laws from Initial Rates

Using the initial rates method and the experimental data, determine the rate law and the value of the rate constant for this reaction:

Equation:



Trial	[NO] (mol/L)	[Cl ₂] (mol/L)	$-\frac{\Delta[\text{NO}]}{\Delta t}$ (mol L ⁻¹ s ⁻¹)
1	0.10	0.10	0.00300
2	0.10	0.15	0.00450
3	0.15	0.10	0.00675

Solution

The rate law for this reaction will have the form:

Equation:

$$\text{rate} = k[\text{NO}]^m[\text{Cl}_2]^n$$

As in [\[link\]](#), we can approach this problem in a stepwise fashion, determining the values of m and n from the experimental data and then using these values to determine the value of k . In this example, however, we will use a different approach to determine the values of m and n :

Equation:	Equation:	Equation:
Determine the value of m from	Using the third	After canceling equivalent
	$\frac{\text{rate 3}}{\text{rate 1}} = \frac{0.00675}{0.00300} = \frac{k(0.15)^m(0.10)^n}{k(0.10)^m(0.10)^n}$	

the data in which $[NO]$ varies and $[Cl_2]$ is constant. We can write the ratios with the subscripts x and y to indicate data from two different trials:

Equation:

Determine the value of n from data in which $[Cl_2]$ varies and $[NO]$ is constant.

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{0.00450}{0.00300} = \frac{k(0.10)^m(0.15)^n}{k(0.10)^m(0.10)^n}$$

Cancelation gives:

Equation:

$$\frac{0.0045}{0.0030} = \frac{(0.15)^n}{(0.10)^n}$$

terms in the numerator and denominator, we are left with:

Equation:

$$1.5 = (1.5)^n$$

Thus n must be 1 and the form of the rate law is:

Equation:

Determine the numerical value of the rate constant k with appropriate units. The units for the rate of reaction are mol/L/s . The units for k are whatever is needed so that substituting into the rate law expression affords the appropriate units for the rate. In this example, the concentration units are mol^3/L^3 . The units for k should be $\text{mol}^{-2}\text{L}^2/\text{s}$ so that the rate is in terms of mol/L/s .

To determine the value of k once the rate law has been solved, simply plug in values from the first experimental trial and solve for k :

$$0.00300 \text{ mol L}^{-1} \text{ s}^{-1} = k(0.10 \text{ mol L}^{-1})^2(0.10 \text{ mol L}^{-1})^1$$

$$k = 3.0 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$$

Check Your Learning

Use the provided initial rate data to derive the rate law for the reaction whose equation is:

Equation:



Trial	[OCl ⁻] (mol/L)	[I ⁻] (mol/L)	Initial Rate (mol/L/s)
1	0.0040	0.0020	0.00184
2	0.0020	0.0040	0.00092
3	0.0020	0.0020	0.00046

Determine the rate law expression and the value of the rate constant k with appropriate units for this reaction.

Note:
Answer:

$$\frac{\text{rate 2}}{\text{rate 3}} = \frac{0.00092}{0.00046} = \frac{k(0.0020)^x(0.0040)^y}{k(0.0020)^x(0.0020)^y}$$

$$2.00 = 2.00^y$$

$$y = 1$$

$$\frac{\text{rate 1}}{\text{rate 2}} = \frac{0.00184}{0.00092} = \frac{k(0.0040)^x(0.0020)^y}{k(0.0020)^x(0.0040)^y}$$

$$2.00 = \frac{2^x}{2^y}$$

$$2.00 = \frac{2^x}{2^1}$$

$$4.00 = 2^x$$

$$x = 2$$
Substituting the concentration data from trial 1 and solving for k yields:

$$\text{rate} = k[\text{OCl}^-]^2[\text{I}^-]^1$$

$$0.00184 = k(0.0040)^2(0.0020)^1$$

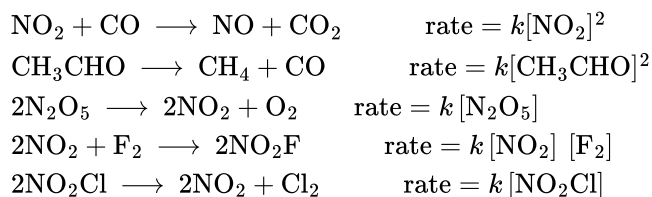
$$k = 5.75 \times 10^4 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$$

Reaction Order and Rate Constant Units

In some of our examples, the reaction orders in the rate law happen to be the same as the coefficients in the chemical equation for the reaction. This is merely a coincidence and very often not the case.

Rate laws may exhibit fractional orders for some reactants, and negative reaction orders are sometimes observed when an increase in the concentration of one reactant causes a decrease in reaction rate. A few examples illustrating these points are provided:

Equation:



It is important to note that *rate laws are determined by experiment only and are not reliably predicted by reaction stoichiometry.*

Reaction orders also play a role in determining the units for the rate constant k . In [\[link\]](#), a second-order reaction, we found the units for k to be $\text{L mol}^{-1} \text{s}^{-1}$, whereas in [\[link\]](#), a third order reaction, we found the units for k to be $\text{mol}^{-2} \text{L}^2/\text{s}$. More generally speaking, the units for the rate constant for a reaction of order $(m + n)$ are $\text{mol}^{1-(m+n)} \text{L}^{(m+n)-1} \text{s}^{-1}$. [\[link\]](#) summarizes the rate constant units for common reaction orders.

Rate Constants for Common Reaction Orders	
Reaction Order	Units of k
$(m + n)$	$\text{mol}^{1-(m+n)} \text{L}^{(m+n)-1} \text{s}^{-1}$
zero	mol/L/s
first	s^{-1}
second	L/mol/s
third	$\text{mol}^{-2} \text{L}^2 \text{s}^{-1}$

Note that the units in the table can also be expressed in terms of molarity (M) instead of mol/L . Also, units of time other than the second (such as minutes, hours, days) may be used, depending on the situation.

Key Concepts and Summary

Rate laws provide a mathematical description of how changes in the concentration of a substance affect the rate of a chemical reaction. Rate laws are determined experimentally and cannot be predicted by reaction stoichiometry. The order of reaction describes how much a change in the concentration of each substance affects the overall rate, and the overall order of a reaction is the sum of the orders for each substance present in the reaction. Reaction orders are typically first order, second order, or zero order, but fractional and even negative orders are possible.

Chemistry End of Chapter Exercises

Exercise:

Problem: How do the rate of a reaction and its rate constant differ?

Exercise:

Problem:

Doubling the concentration of a reactant increases the rate of a reaction four times. With this knowledge, answer the following questions:

- What is the order of the reaction with respect to that reactant?
- Tripling the concentration of a different reactant increases the rate of a reaction three times. What is the order of the reaction with respect to that reactant?

Solution:

- (a) 2; (b) 1

Exercise:**Problem:**

Tripling the concentration of a reactant increases the rate of a reaction nine times. With this knowledge, answer the following questions:

- (a) What is the order of the reaction with respect to that reactant?
- (b) Increasing the concentration of a reactant by a factor of four increases the rate of a reaction four times. What is the order of the reaction with respect to that reactant?

Exercise:**Problem:**

How much and in what direction will each of the following affect the rate of the reaction:



- (a) Decreasing the pressure of NO_2 from 0.50 atm to 0.250 atm.
- (b) Increasing the concentration of CO from 0.01 M to 0.03 M.

Solution:

- (a) The process reduces the rate by a factor of 4. (b) Since CO does not appear in the rate law, the rate is not affected.

Exercise:**Problem:**

How will each of the following affect the rate of the reaction: $\text{CO}(g) + \text{NO}_2(g) \longrightarrow \text{CO}_2(g) + \text{NO}(g)$ if the rate law for the reaction is $\text{rate} = k[\text{NO}_2][\text{CO}]$?

- (a) Increasing the pressure of NO_2 from 0.1 atm to 0.3 atm
- (b) Increasing the concentration of CO from 0.02 M to 0.06 M.

Exercise:**Problem:**

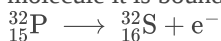
Regular flights of supersonic aircraft in the stratosphere are of concern because such aircraft produce nitric oxide, NO, as a byproduct in the exhaust of their engines. Nitric oxide reacts with ozone, and it has been suggested that this could contribute to depletion of the ozone layer. The reaction $\text{NO} + \text{O}_3 \longrightarrow \text{NO}_2 + \text{O}_2$ is first order with respect to both NO and O_3 with a rate constant of $2.20 \times 10^7 \text{ L/mol}\cdot\text{s}$. What is the instantaneous rate of disappearance of NO when $[\text{NO}] = 3.3 \times 10^{-6} \text{ M}$ and $[\text{O}_3] = 5.9 \times 10^{-7} \text{ M}$?

Solution:

$$4.3 \times 10^{-5} \text{ mol/L}\cdot\text{s}$$

Exercise:**Problem:**

Radioactive phosphorus is used in the study of biochemical reaction mechanisms because phosphorus atoms are components of many biochemical molecules. The location of the phosphorus (and the location of the molecule it is bound in) can be detected from the electrons (beta particles) it produces:



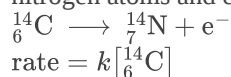
$$\text{Rate} = 4.85 \times 10^{-2} \text{ day}^{-1} [{}^{32}\text{P}]$$

What is the instantaneous rate of production of electrons in a sample with a phosphorus concentration of 0.0033 M ?

Exercise:

Problem:

The rate constant for the radioactive decay of ^{14}C is $1.21 \times 10^{-4}\text{ year}^{-1}$. The products of the decay are nitrogen atoms and electrons (beta particles):



What is the instantaneous rate of production of N atoms in a sample with a carbon-14 content of $6.5 \times 10^{-9}\text{ M}$?

Solution:

$$7.9 \times 10^{-13}\text{ mol/L/year}$$

Exercise:

Problem:

The decomposition of acetaldehyde is a second order reaction with a rate constant of $4.71 \times 10^{-8}\text{ L/mol/s}$. What is the instantaneous rate of decomposition of acetaldehyde in a solution with a concentration of $5.55 \times 10^{-4}\text{ M}$?

Exercise:

Problem:

Alcohol is removed from the bloodstream by a series of metabolic reactions. The first reaction produces acetaldehyde; then other products are formed. The following data have been determined for the rate at which alcohol is removed from the blood of an average male, although individual rates can vary by 25–30%. Women metabolize alcohol a little more slowly than men:

$[\text{C}_2\text{H}_5\text{OH}]\text{ (M)}$	4.4×10^{-2}	3.3×10^{-2}	2.2×10^{-2}
Rate (mol/L/h)	2.0×10^{-2}	2.0×10^{-2}	2.0×10^{-2}

Determine the rate equation, the rate constant, and the overall order for this reaction.

Solution:

$\text{rate} = k$; $k = 2.0 \times 10^{-2}\text{ mol/L/h}$ (about 0.9 g/L/h for the average male); The reaction is zero order.

Exercise:

Problem:

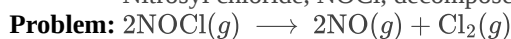
Under certain conditions the decomposition of ammonia on a metal surface gives the following data:

$[\text{NH}_3] \text{ (M)}$	1.0×10^{-3}	2.0×10^{-3}	3.0×10^{-3}
Rate (mol/L/h ¹)	1.5×10^{-6}	1.5×10^{-6}	1.5×10^{-6}

Determine the rate equation, the rate constant, and the overall order for this reaction.

Exercise:

Nitrosyl chloride, NOCl, decomposes to NO and Cl₂.



Determine the rate equation, the rate constant, and the overall order for this reaction from the following data:

$[\text{NOCl}] \text{ (M)}$	0.10	0.20	0.30
Rate (mol/L/h)	8.0×10^{-10}	3.2×10^{-9}	7.2×10^{-9}

Solution:

rate = $k[\text{NOCl}]^2$; $k = 8.0 \times 10^{-8} \text{ L/mol/h}$; second order

Exercise:

Problem:

From the following data, determine the rate equation, the rate constant, and the order with respect to A for the reaction $A \longrightarrow 2C$.

$[A] \text{ (M)}$	1.33×10^{-2}	2.66×10^{-2}	3.99×10^{-2}
Rate (mol/L/h)	3.80×10^{-7}	1.52×10^{-6}	3.42×10^{-6}

Exercise:

Nitrogen monoxide reacts with chlorine according to the equation:



The following initial rates of reaction have been observed for certain reactant concentrations:

--

[NO] (mol/L ¹)	[Cl ₂] (mol/L)	Rate (mol/L/h)
0.50	0.50	1.14
1.00	0.50	4.56
1.00	1.00	9.12

What is the rate equation that describes the rate's dependence on the concentrations of NO and Cl₂? What is the rate constant? What are the orders with respect to each reactant?

Solution:

rate = $k[\text{NO}]^2[\text{Cl}_2]$; $k = 9.1 \text{ L}^2 \text{ mol}^{-2} \text{ h}^{-1}$; second order in NO; first order in Cl₂

Exercise:

Problem:

Hydrogen reacts with nitrogen monoxide to form dinitrogen monoxide (laughing gas) according to the equation: $\text{H}_2(g) + 2\text{NO}(g) \longrightarrow \text{N}_2\text{O}(g) + \text{H}_2\text{O}(g)$

Determine the rate equation, the rate constant, and the orders with respect to each reactant from the following data:

[NO] (M)	0.30	0.60	0.60
[H ₂] (M)	0.35	0.35	0.70
Rate (mol/L/s)	2.835×10^{-3}	1.134×10^{-2}	2.268×10^{-2}

Exercise:

Problem: For the reaction $A \longrightarrow B + C$, the following data were obtained at 30 °C:

[A] (M)	0.230	0.356	0.557
Rate (mol/L/s)	4.17×10^{-4}	9.99×10^{-4}	2.44×10^{-3}

(a) What is the order of the reaction with respect to [A], and what is the rate equation?

(b) What is the rate constant?

Solution:

(a) The rate equation is second order in A and is written as $\text{rate} = k[A]^2$. (b) $k = 7.88 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$

Exercise:

Problem: For the reaction $Q \longrightarrow W + X$, the following data were obtained at 30 °C:

[Q] _{initial} (M)	0.170	0.212	0.357
Rate (mol/L/s)	6.68×10^{-3}	1.04×10^{-2}	2.94×10^{-2}

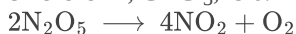
(a) What is the order of the reaction with respect to [Q], and what is the rate equation?

(b) What is the rate constant?

Exercise:

Problem:

The rate constant for the first-order decomposition at 45 °C of dinitrogen pentoxide, N_2O_5 , dissolved in chloroform, CHCl_3 , is $6.2 \times 10^{-4} \text{ min}^{-1}$.



What is the rate of the reaction when $[\text{N}_2\text{O}_5] = 0.40 \text{ M}$?

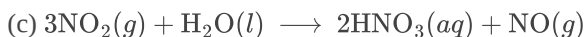
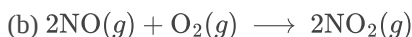
Solution:

(a) $2.5 \times 10^{-4} \text{ mol/L/min}$

Exercise:

Problem:

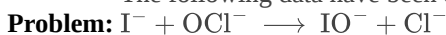
The annual production of HNO_3 in 2013 was 60 million metric tons. Most of that was prepared by the following sequence of reactions, each run in a separate reaction vessel.



The first reaction is run by burning ammonia in air over a platinum catalyst. This reaction is fast. The reaction in equation (c) is also fast. The second reaction limits the rate at which nitric acid can be prepared from ammonia. If equation (b) is second order in NO and first order in O_2 , what is the rate of formation of NO_2 when the oxygen concentration is 0.50 M and the nitric oxide concentration is 0.75 M? The rate constant for the reaction is $5.8 \times 10^{-6} \text{ L}^2/\text{mol}^2/\text{s}$.

Exercise:

The following data have been determined for the reaction:



	1	2	3
$[\text{I}^-]_{\text{initial}} (M)$	0.10	0.20	0.30
$[\text{OCl}^-]_{\text{initial}} (M)$	0.050	0.050	0.010
Rate (mol/L/s)	3.05×10^{-4}	6.20×10^{-4}	1.83×10^{-4}

Determine the rate equation and the rate constant for this reaction.

Solution:

$$\text{rate} = k[\text{I}^-][\text{OCl}^-]; k = 6.1 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$$

Glossary

method of initial rates

use of a more explicit algebraic method to determine the orders in a rate law

overall reaction order

sum of the reaction orders for each substance represented in the rate law

rate constant (k)

proportionality constant in the relationship between reaction rate and concentrations of reactants

rate law

(also, rate equation) mathematical equation showing the dependence of reaction rate on the rate constant and the concentration of one or more reactants

reaction order

value of an exponent in a rate law, expressed as an ordinal number (for example, zero order for 0, first order for 1, second order for 2, and so on)

Integrated Rate Laws

By the end of this section, you will be able to:

- Explain the form and function of an integrated rate law
- Perform integrated rate law calculations for zero-, first-, and second-order reactions
- Define half-life and carry out related calculations
- Identify the order of a reaction from concentration/time data

The rate laws we have seen thus far relate the rate and the concentrations of reactants. We can also determine a second form of each rate law that relates the concentrations of reactants and time. These are called **integrated rate laws**. We can use an integrated rate law to determine the amount of reactant or product present after a period of time or to estimate the time required for a reaction to proceed to a certain extent. For example, an integrated rate law is used to determine the length of time a radioactive material must be stored for its radioactivity to decay to a safe level.

Using calculus, the differential rate law for a chemical reaction can be integrated with respect to time to give an equation that relates the amount of reactant or product present in a reaction mixture to the elapsed time of the reaction. This process can either be very straightforward or very complex, depending on the complexity of the differential rate law. For purposes of discussion, we will focus on the resulting integrated rate laws for first-, second-, and zero-order reactions.

First-Order Reactions

An equation relating the rate constant k to the initial concentration $[A]_0$ and the concentration $[A]_t$ present after any given time t can be derived for a first-order reaction and shown to be:

Equation:

$$\ln \left(\frac{[A]_t}{[A]_0} \right) = -kt$$

or

Equation:

$$\ln \left(\frac{[A]_0}{[A]_t} \right) = kt$$

or

Equation:

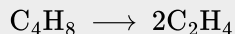
$$[A] = [A]_0 e^{-kt}$$

Example:

The Integrated Rate Law for a First-Order Reaction

The rate constant for the first-order decomposition of cyclobutane, C_4H_8 at 500 °C is $9.2 \times 10^{-3} \text{ s}^{-1}$:

Equation:



How long will it take for 80.0% of a sample of C_4H_8 to decompose?

Solution

We use the integrated form of the rate law to answer questions regarding time:

Equation:

$$\ln \left(\frac{[A]_0}{[A]} \right) = kt$$

There are four variables in the rate law, so if we know three of them, we can determine the fourth. In this case we know $[A]_0$, $[A]$, and k , and need to find t .

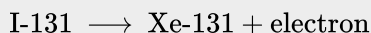
The initial concentration of C_4H_8 , $[A]_0$, is not provided, but the provision that 80.0% of the sample has decomposed is enough information to solve this problem. Let x be the initial concentration, in which case the concentration after 80.0% decomposition is 20.0% of x or $0.200x$. Rearranging the rate law to isolate t and substituting the provided quantities yields:

Equation:

$$\begin{aligned} t &= \ln \frac{[x]}{[0.200x]} \times \frac{1}{k} \\ &= \ln \frac{0.100 \text{ mol L}^{-1}}{0.020 \text{ mol L}^{-1}} \times \frac{1}{9.2 \times 10^{-3} \text{ s}^{-1}} \\ &= 1.609 \times \frac{1}{9.2 \times 10^{-3} \text{ s}^{-1}} \\ &= 1.7 \times 10^2 \text{ s} \end{aligned}$$

Check Your Learning

Iodine-131 is a radioactive isotope that is used to diagnose and treat some forms of thyroid cancer. Iodine-131 decays to xenon-131 according to the equation:

Equation:

The decay is first-order with a rate constant of 0.138 d^{-1} . All radioactive decay is first order. How many days will it take for 90% of the iodine-131 in a 0.500 M solution of this substance to decay to Xe-131?

Note:**Answer:**

16.7 days

We can use integrated rate laws with experimental data that consist of time and concentration information to determine the order and rate constant of a reaction. The integrated rate law can be rearranged to a standard linear equation format:

Equation:

$$\begin{aligned} \ln [A] &= (-k)(t) + \ln [A]_0 \\ y &= mx + b \end{aligned}$$

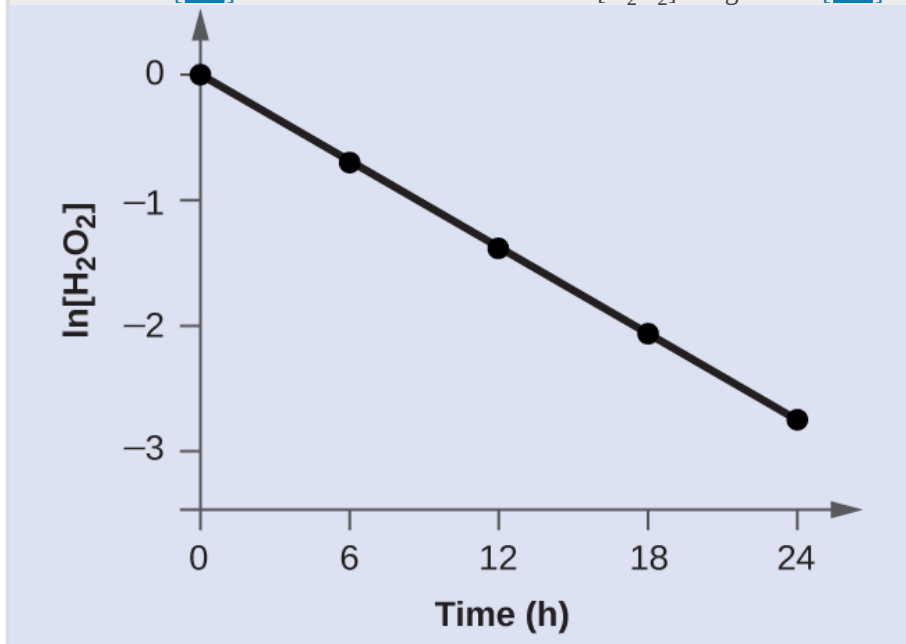
A plot of $\ln[A]$ versus t for a first-order reaction is a straight line with a slope of $-k$ and an intercept of $\ln[A]_0$. If a set of rate data are plotted in this fashion but do *not* result in a straight line, the reaction is not first order in A .

Example:**Determination of Reaction Order by Graphing**

Show that the data in [\[link\]](#) can be represented by a first-order rate law by graphing $\ln[\text{H}_2\text{O}_2]$ versus time. Determine the rate constant for the rate of decomposition of H_2O_2 from this data.

Solution

The data from [\[link\]](#) with the addition of values of $\ln[\text{H}_2\text{O}_2]$ are given in [\[link\]](#).



The linear relationship between the $\ln[\text{H}_2\text{O}_2]$ and time shows that the decomposition of hydrogen peroxide is a first-order reaction.

Trial	Time (h)	$[\text{H}_2\text{O}_2]$ (M)	$\ln[\text{H}_2\text{O}_2]$
1	0	1.000	0.0
2	6.00	0.500	-0.693
3	12.00	0.250	-1.386
4	18.00	0.125	-2.079
5	24.00	0.0625	-2.772

The plot of $\ln[\text{H}_2\text{O}_2]$ versus time is linear, thus we have verified that the reaction may be described by a first-order rate law.

The rate constant for a first-order reaction is equal to the negative of the slope of the plot of $\ln[\text{H}_2\text{O}_2]$ versus time where:

Equation:

$$\text{slope} = \frac{\text{change in } y}{\text{change in } x} = \frac{\Delta y}{\Delta x} = \frac{\Delta \ln [\text{H}_2\text{O}_2]}{\Delta t}$$

In order to determine the slope of the line, we need two values of $\ln[\text{H}_2\text{O}_2]$ at different values of t (one near each end of the line is preferable). For example, the value of $\ln[\text{H}_2\text{O}_2]$ when t is 6.00 h is -0.693 ; the value when $t = 12.00$ h is -1.386 :

Equation:

$$\begin{aligned}\text{slope} &= \frac{-1.386 - (-0.693)}{12.00 \text{ h} - 6.00 \text{ h}} \\ &= \frac{-0.693}{6.00 \text{ h}} \\ &= -1.155 \times 10^{-1} \text{ h}^{-1} \\ k &= -\text{slope} = -(-1.155 \times 10^{-1} \text{ h}^{-1}) = 1.155 \times 10^{-1} \text{ h}^{-1}\end{aligned}$$

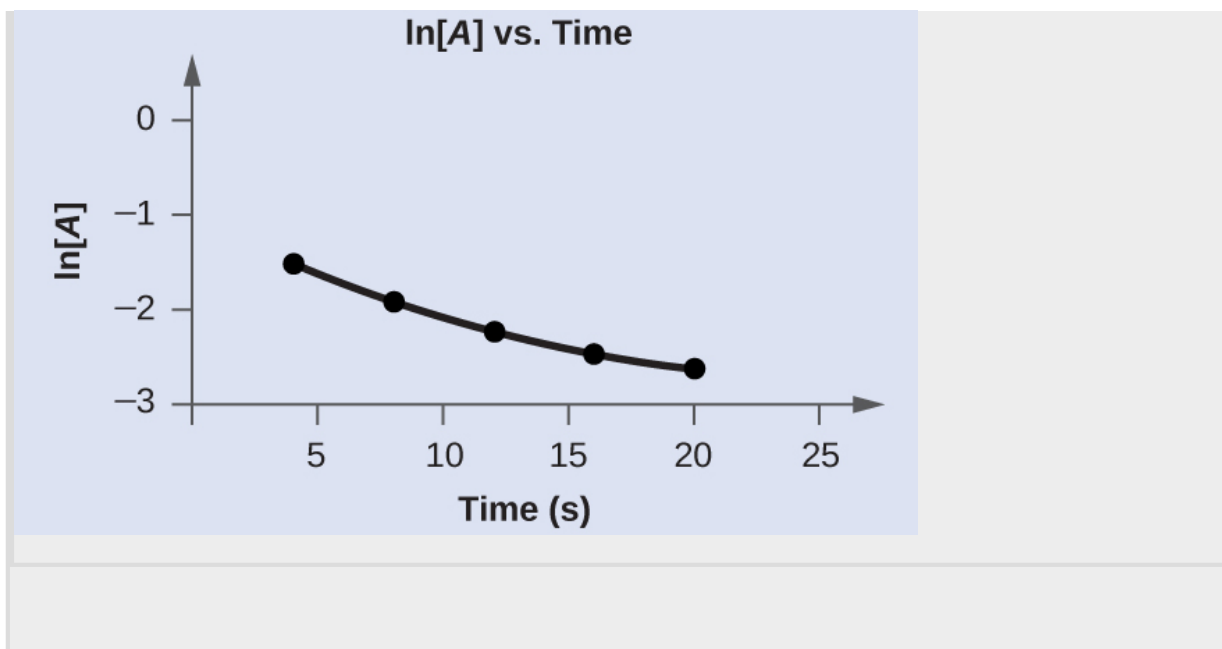
Check Your Learning

Graph the following data to determine whether the reaction $A \rightarrow B + C$ is first order.

Trial	Time (s)	[A]
1	4.0	0.220
2	8.0	0.144
3	12.0	0.110
4	16.0	0.088
5	20.0	0.074

Note:**Answer:**

The plot of $\ln[A]$ vs. t is not a straight line. The equation is not first order:



Second-Order Reactions

The equations that relate the concentrations of reactants and the rate constant of second-order reactions are fairly complicated. We will limit ourselves to the simplest second-order reactions, namely, those with rates that are dependent upon just one reactant's concentration and described by the differential rate law:

Equation:

$$\text{Rate} = k[A]^2$$

For these second-order reactions, the integrated rate law is:

Equation:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

where the terms in the equation have their usual meanings as defined earlier.

Example:

The Integrated Rate Law for a Second-Order Reaction

The reaction of butadiene gas (C_4H_6) with itself produces C_8H_{12} gas as follows:

Equation:



The reaction is second order with a rate constant equal to $5.76 \times 10^{-2} \text{ L/mol/min}$ under certain conditions. If the initial concentration of butadiene is 0.200 M , what is the concentration remaining after 10.0 min ?

Solution

We use the integrated form of the rate law to answer questions regarding time. For a second-order reaction, we have:

Equation:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

We know three variables in this equation: $[A]_0 = 0.200 \text{ mol/L}$, $k = 5.76 \times 10^{-2} \text{ L/mol/min}$, and $t = 10.0 \text{ min}$. Therefore, we can solve for $[A]$, the fourth variable:

Equation:

$$\begin{aligned}\frac{1}{[A]} &= (5.76 \times 10^{-2} \text{ L mol}^{-1} \text{ min}^{-1}) (10 \text{ min}) + \frac{1}{0.200 \text{ mol}^{-1}} \\ \frac{1}{[A]} &= (5.76 \times 10^{-1} \text{ L mol}^{-1}) + 5.00 \text{ L mol}^{-1} \\ \frac{1}{[A]} &= 5.58 \text{ L mol}^{-1} \\ [A] &= 1.79 \times 10^{-1} \text{ mol L}^{-1}\end{aligned}$$

Therefore 0.179 mol/L of butadiene remain at the end of 10.0 min, compared to the 0.200 mol/L that was originally present.

Check Your Learning

If the initial concentration of butadiene is 0.0200 M, what is the concentration remaining after 20.0 min?

Note:

Answer:

0.0195 mol/L

The integrated rate law for our second-order reactions has the form of the equation of a straight line:

Equation:

$$\begin{aligned}\frac{1}{[A]} &= kt + \frac{1}{[A]_0} \\ y &= mx + b\end{aligned}$$

A plot of $\frac{1}{[A]}$ versus t for a second-order reaction is a straight line with a slope of k and an intercept of $\frac{1}{[A]_0}$. If the plot is not a straight line, then the reaction is not second order.

Example:

Determination of Reaction Order by Graphing

The data below are for the same reaction described in [\[link\]](#). Test these data to confirm that this dimerization reaction is second-order.

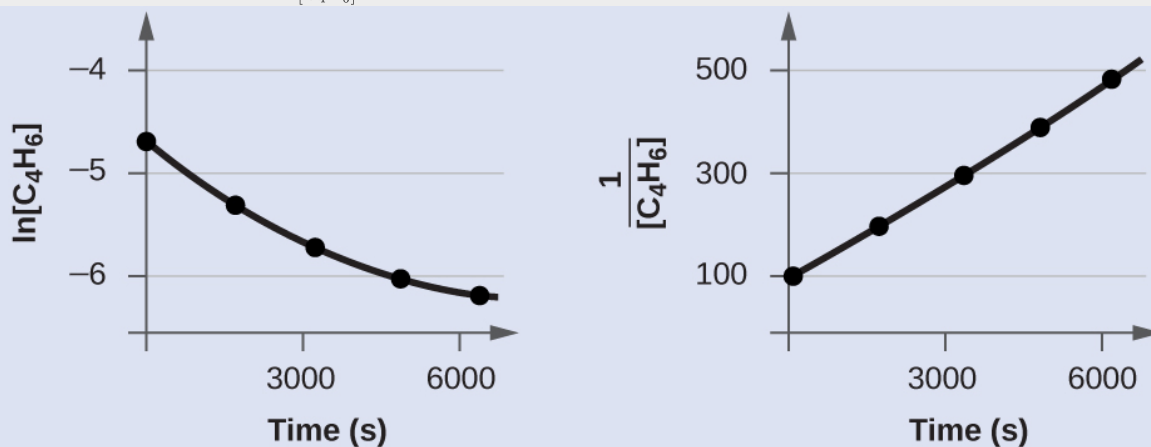
Solution

Trial	Time (s)	$[\text{C}_4\text{H}_6] \text{ (M)}$
1	0	1.00×10^{-2}
2	1600	5.04×10^{-3}
3	3200	3.37×10^{-3}
4	4800	2.53×10^{-3}
5	6200	2.08×10^{-3}

In order to distinguish a first-order reaction from a second-order reaction, we plot $\ln[\text{C}_4\text{H}_6]$ versus t and compare it with a plot of $\frac{1}{[\text{C}_4\text{H}_6]}$ versus t . The values needed for these plots follow.

Time (s)	$\frac{1}{[\text{C}_4\text{H}_6]} \text{ (M}^{-1}\text{)}$	$\ln[\text{C}_4\text{H}_6]$
0	100	-4.605
1600	198	-5.289
3200	296	-5.692
4800	395	-5.978
6200	481	-6.175

The plots are shown in [\[link\]](#). As you can see, the plot of $\ln[\text{C}_4\text{H}_6]$ versus t is not linear, therefore the reaction is not first order. The plot of $\frac{1}{[\text{C}_4\text{H}_6]}$ versus t is linear, indicating that the reaction is second order.



These two graphs show first- and second-order plots for the dimerization of C_4H_6 . Since the first-order plot (left) is not linear, we know that the reaction is not first order. The linear trend in the second-order

plot (right) indicates that the reaction follows second-order kinetics.

Check Your Learning

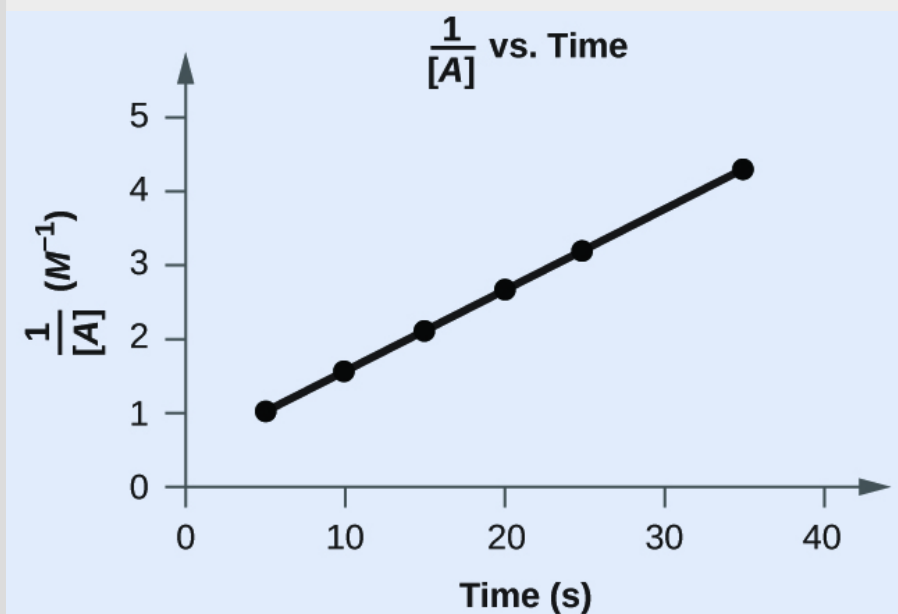
Does the following data fit a second-order rate law?

Trial	Time (s)	[A] (M)
1	5	0.952
2	10	0.625
3	15	0.465
4	20	0.370
5	25	0.308
6	35	0.230

Note:

Answer:

Yes. The plot of $\frac{1}{[A]}$ vs. t is linear:



Zero-Order Reactions

For zero-order reactions, the differential rate law is:

Equation:

$$\text{Rate} = k[A]^0 = k$$

A zero-order reaction thus exhibits a constant reaction rate, regardless of the concentration of its reactants.

The integrated rate law for a zero-order reaction also has the form of the equation of a straight line:

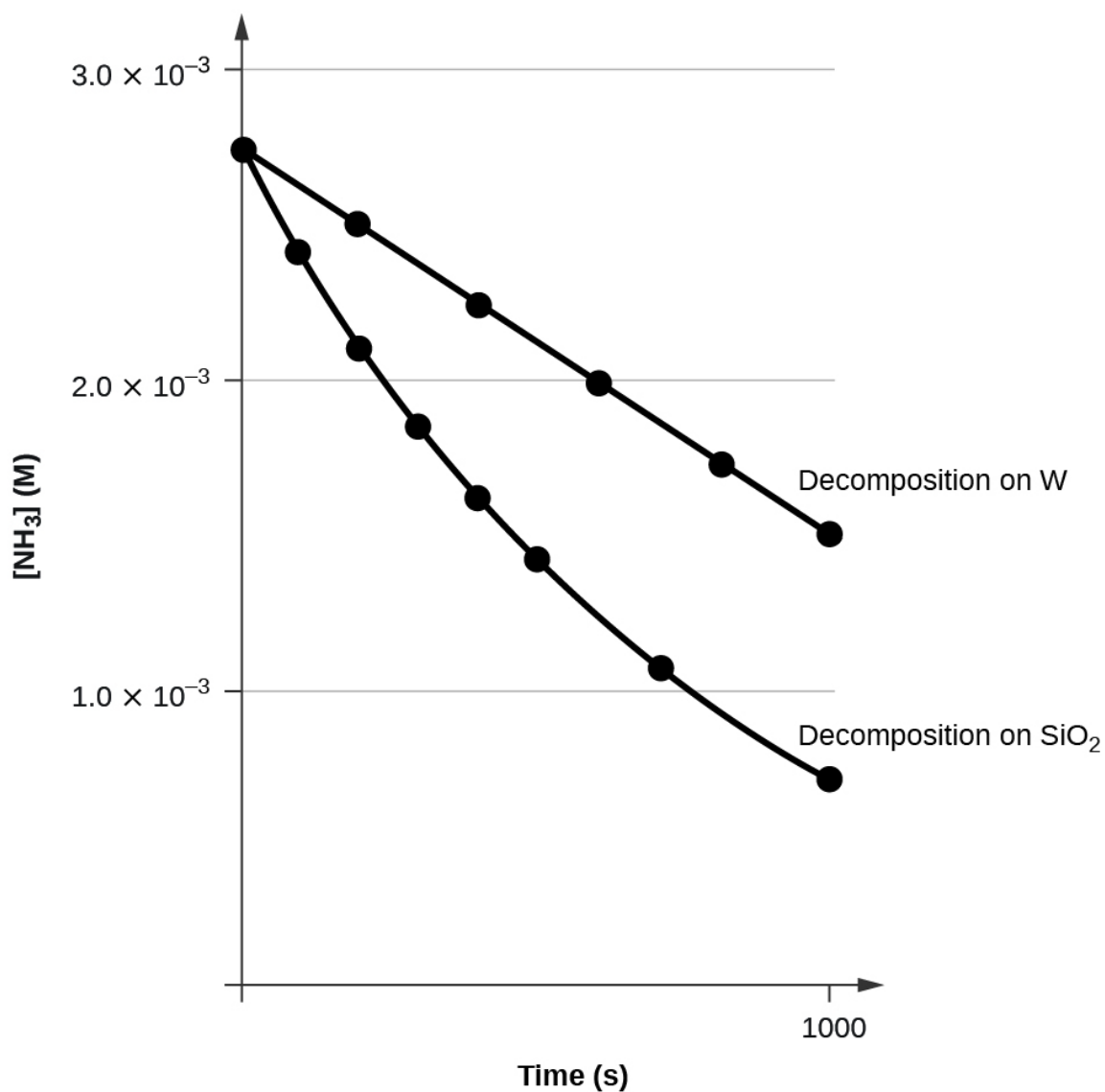
Equation:

$$\begin{aligned}[A] &= -kt + [A]_0 \\ y &= mx + b\end{aligned}$$

A plot of $[A]$ versus t for a zero-order reaction is a straight line with a slope of $-k$ and an intercept of $[A]_0$. [\[link\]](#) shows a plot of $[\text{NH}_3]$ versus t for the decomposition of ammonia on a hot tungsten wire and for the decomposition of ammonia on hot quartz (SiO_2). The decomposition of NH_3 on hot tungsten is zero order; the plot is a straight line. The decomposition of NH_3 on hot quartz is not zero order (it is first order). From the slope of the line for the zero-order decomposition, we can determine the rate constant:

Equation:

$$\text{slope} = -k = 1.3110^{-6} \text{ mol/L/s}$$



The decomposition of NH_3 on a tungsten (W) surface is a zero-order reaction, whereas on a quartz (SiO_2) surface, the reaction is first order.

The Half-Life of a Reaction

The **half-life of a reaction** ($t_{1/2}$) is the time required for one-half of a given amount of reactant to be consumed. In each succeeding half-life, half of the remaining concentration of the reactant is consumed. Using the decomposition of hydrogen peroxide ([link](#)) as an example, we find that during the first half-life (from 0.00 hours to 6.00 hours), the concentration of H_2O_2 decreases from 1.000 M to 0.500 M. During the second half-life (from 6.00 hours to 12.00 hours), it decreases from 0.500 M to 0.250 M; during the third half-life, it decreases from 0.250 M to 0.125 M. The concentration of H_2O_2 decreases by half during each successive period of 6.00 hours. The decomposition of hydrogen peroxide is a first-order reaction, and, as can

be shown, the half-life of a first-order reaction is independent of the concentration of the reactant. However, half-lives of reactions with other orders depend on the concentrations of the reactants.

First-Order Reactions

We can derive an equation for determining the half-life of a first-order reaction from the alternate form of the integrated rate law as follows:

Equation:

$$\ln \frac{[A]_0}{[A]} = kt$$
$$t = \ln \frac{[A]_0}{[A]} \times \frac{1}{k}$$

If we set the time t equal to the half-life, $t_{1/2}$, the corresponding concentration of A at this time is equal to one-half of its initial concentration. Hence, when $t = t_{1/2}$, $[A] = \frac{1}{2}[A]_0$.

Therefore:

Equation:

$$t_{1/2} = \ln \frac{[A]_0}{\frac{1}{2}[A]_0} \times \frac{1}{k}$$
$$= \ln 2 \times \frac{1}{k} = 0.693 \times \frac{1}{k}$$

Thus:

Equation:

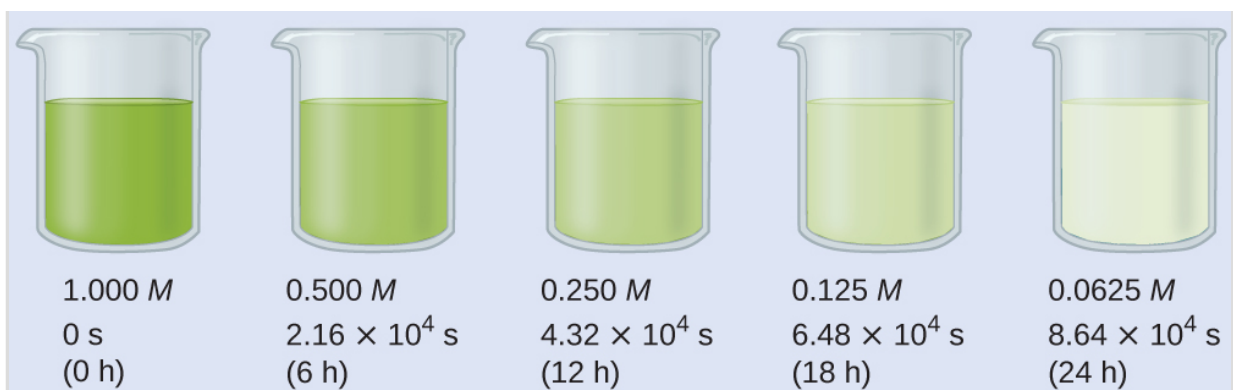
$$t_{1/2} = \frac{0.693}{k}$$

We can see that the half-life of a first-order reaction is inversely proportional to the rate constant k . A fast reaction (shorter half-life) will have a larger k ; a slow reaction (longer half-life) will have a smaller k .

Example:

Calculation of a First-order Rate Constant using Half-Life

Calculate the rate constant for the first-order decomposition of hydrogen peroxide in water at 40 °C, using the data given in [\[link\]](#).



The decomposition of H_2O_2 ($2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$) at 40°C is illustrated. The intensity of the color symbolizes the concentration of H_2O_2 at the indicated times; H_2O_2 is actually colorless.

Solution

The half-life for the decomposition of H_2O_2 is 2.16×10^4 s:

Equation:

$$t_{1/2} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.16 \times 10^4 \text{ s}} = 3.21 \times 10^{-5} \text{ s}^{-1}$$

Check Your Learning

The first-order radioactive decay of iodine-131 exhibits a rate constant of 0.138 d^{-1} . What is the half-life for this decay?

Note:

Answer:

5.02 d.

Second-Order Reactions

We can derive the equation for calculating the half-life of a second order as follows:

Equation:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

or

Equation:

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

If

Equation:

$$t = t_{1/2}$$

then

Equation:

$$[A] = \frac{1}{2}[A]_0$$

and we can write:

Equation:

$$\begin{aligned}\frac{1}{\frac{1}{2}[A]_0} - \frac{1}{[A]_0} &= kt_{1/2} \\ 2[A]_0 - \frac{1}{[A]_0} &= kt_{1/2} \\ \frac{1}{[A]_0} &= kt_{1/2}\end{aligned}$$

Thus:

Equation:

$$t_{1/2} = \frac{1}{k[A]_0}$$

For a second-order reaction, $t_{1/2}$ is inversely proportional to the concentration of the reactant, and the half-life increases as the reaction proceeds because the concentration of reactant decreases. Consequently, we find the use of the half-life concept to be more complex for second-order reactions than for first-order reactions. Unlike with first-order reactions, the rate constant of a second-order reaction cannot be calculated directly from the half-life unless the initial concentration is known.

Zero-Order Reactions

We can derive an equation for calculating the half-life of a zero order reaction as follows:

Equation:

$$[A] = -kt + [A]_0$$

When half of the initial amount of reactant has been consumed $t = t_{1/2}$ and $[A] = \frac{[A]_0}{2}$. Thus:

Equation:

$$\begin{aligned}\frac{[A]_0}{2} &= -kt_{1/2} + [A]_0 \\ kt_{1/2} &= \frac{[A]_0}{2}\end{aligned}$$

and

Equation:

$$t_{1/2} = \frac{[A]_0}{2k}$$

The half-life of a zero-order reaction increases as the initial concentration increases.

Equations for both differential and integrated rate laws and the corresponding half-lives for zero-, first-, and second-order reactions are summarized in [\[link\]](#).

Summary of Rate Laws for Zero-, First-, and Second-Order Reactions			
	Zero-Order	First-Order	Second-Order
rate law	rate = k	rate = $k[A]$	rate = $k[A]^2$
units of rate constant	$M\ s^{-1}$	s^{-1}	$M^{-1}\ s^{-1}$
integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \left(\frac{1}{[A]_0}\right)$
plot needed for linear fit of rate data	$[A]$ vs. t	$\ln[A]$ vs. t	$\frac{1}{[A]}$ vs. t
relationship between slope of linear plot and rate constant	$k = -\text{slope}$	$k = -\text{slope}$	$k = +\text{slope}$
half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{[A]_0 k}$

Key Concepts and Summary

Integrated rate laws are determined by integration of the corresponding differential rate laws. Rate constants for those rate laws are determined from measurements of concentration at various times during a reaction.

The half-life of a reaction is the time required to decrease the amount of a given reactant by one-half. The half-life of a zero-order reaction decreases as the initial concentration of the reactant in the reaction decreases. The half-life of a first-order reaction is independent of concentration, and the half-life of a second-order reaction decreases as the concentration increases.

Key Equations

- integrated rate law for zero-order reactions: $[A] = -kt + [A]_0$, $t_{1/2} = \frac{[A]_0}{2k}$
- integrated rate law for first-order reactions: $\ln[A] = -kt + \ln[A]_0$, $t_{1/2} = \frac{0.693}{k}$
- integrated rate law for second-order reactions: $\frac{1}{[A]} = kt + \frac{1}{[A]_0}$, $t_{1/2} = \frac{1}{[A]_0 k}$

Chemistry End of Chapter Exercises

Exercise:**Problem:**

Describe how graphical methods can be used to determine the order of a reaction and its rate constant from a series of data that includes the concentration of A at varying times.

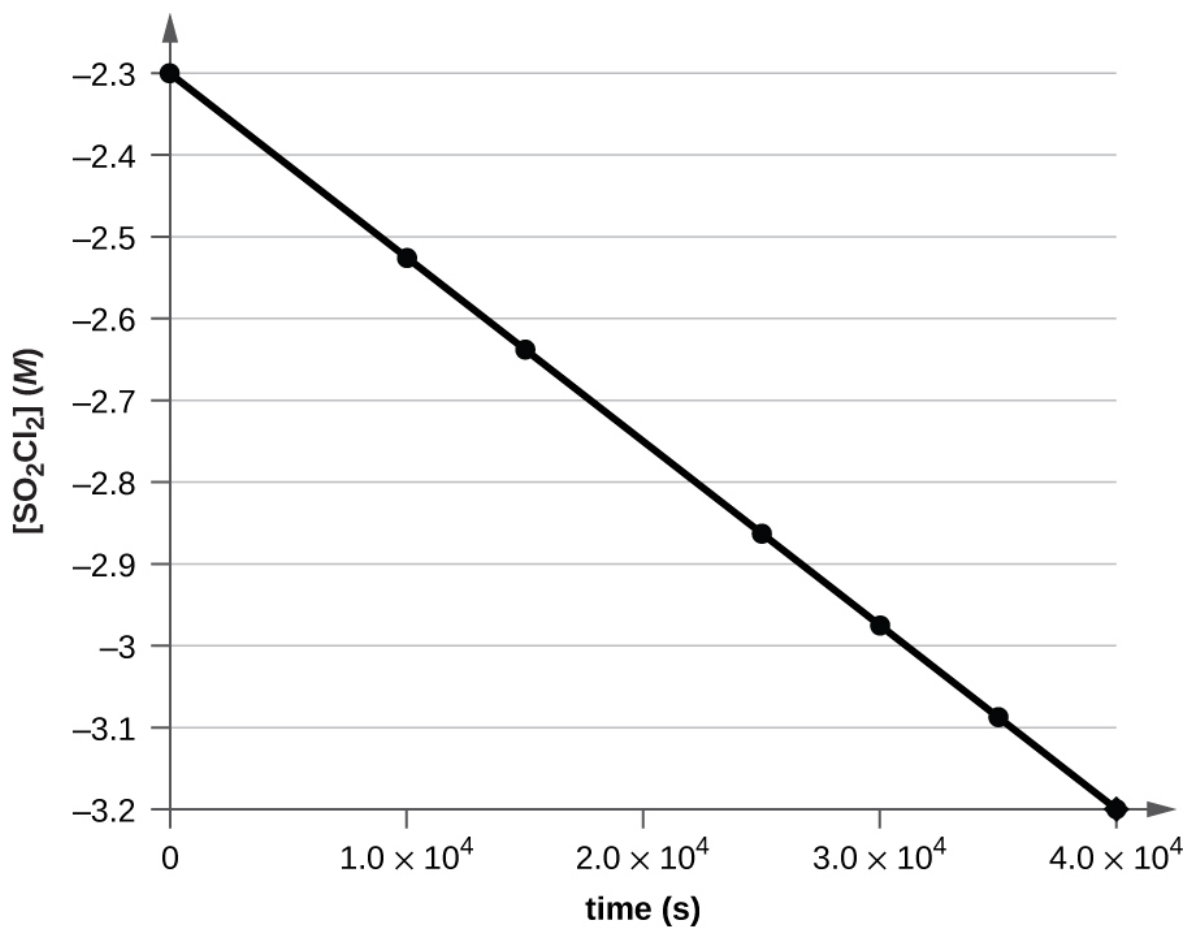
Exercise:**Problem:**

Use the data provided to graphically determine the order and rate constant of the following reaction:
 $\text{SO}_2\text{Cl}_2 \longrightarrow \text{SO}_2 + \text{Cl}_2$

Time (s)	0	5.00×10^3	1.00×10^4	1.50×10^4
$[\text{SO}_2\text{Cl}_2]$ (M)	0.100	0.0896	0.0802	0.0719
Time (s)	2.50×10^4	3.00×10^4	4.00×10^4	
$[\text{SO}_2\text{Cl}_2]$ (M)	0.0577	0.0517	0.0415	

Solution:

Plotting a graph of $\ln[\text{SO}_2\text{Cl}_2]$ versus t reveals a linear trend; therefore we know this is a first-order reaction:

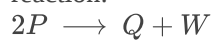


$$k = -2.20 \times 10^5 \text{ s}^{-1}$$

Exercise:

Problem:

Use the data provided in a graphical method to determine the order and rate constant of the following reaction:



Time (s)	9.0	13.0	18.0	22.0	25.0
[P] (M)	1.077×10^{-3}	1.068×10^{-3}	1.055×10^{-3}	1.046×10^{-3}	1.039×10^{-3}

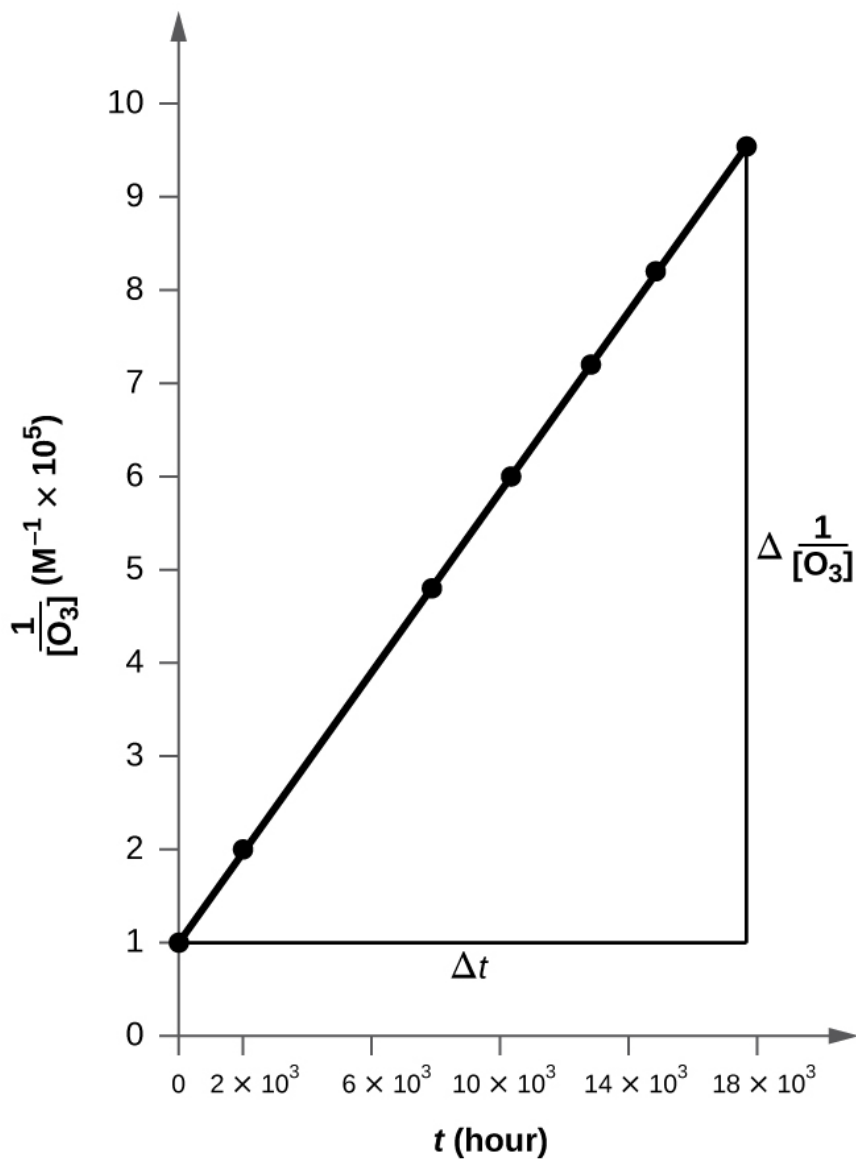
Exercise:

Problem:

Pure ozone decomposes slowly to oxygen, $2\text{O}_3(g) \longrightarrow 3\text{O}_2(g)$. Use the data provided in a graphical method and determine the order and rate constant of the reaction.

Time (h)	0	2.0×10^3	7.6×10^3	1.00×10^4
$[\text{O}_3] (M)$	1.00×10^{-5}	4.98×10^{-6}	2.07×10^{-6}	1.66×10^{-6}
Time (h)	1.23×10^4	1.43×10^4	1.70×10^4	
$[\text{O}_3] (M)$	1.39×10^{-6}	1.22×10^{-6}	1.05×10^{-6}	

Solution:

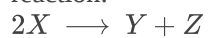


The plot is nicely linear, so the reaction is second order.
 $k = 50.1 \text{ L mol}^{-1} \text{ h}^{-1}$

Exercise:

Problem:

From the given data, use a graphical method to determine the order and rate constant of the following reaction:



Time (s)	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0
[X] (M)	0.0990	0.0497	0.0332	0.0249	0.0200	0.0166	0.0143	0.0125

Exercise:

Problem:

What is the half-life for the first-order decay of phosphorus-32? ($^{32}_{15}\text{P} \longrightarrow ^{32}_{16}\text{S} + \text{e}^-$) The rate constant for the decay is $4.85 \times 10^{-2} \text{ day}^{-1}$.

Solution:

14.3 d

Exercise:

Problem:

What is the half-life for the first-order decay of carbon-14? ($^{14}_6\text{C} \longrightarrow ^{14}_7\text{N} + \text{e}^-$) The rate constant for the decay is $1.21 \times 10^{-4} \text{ year}^{-1}$.

Exercise:

Problem:

What is the half-life for the decomposition of NOCl when the concentration of NOCl is 0.15 M? The rate constant for this second-order reaction is $8.0 \times 10^{-8} \text{ L/mol/s}$.

Solution:

$8.3 \times 10^7 \text{ s}$

Exercise:

Problem:

What is the half-life for the decomposition of O_3 when the concentration of O_3 is $2.35 \times 10^{-6} \text{ M}$? The rate constant for this second-order reaction is 50.4 L/mol/h.

Exercise:

Problem:

The reaction of compound A to give compounds C and D was found to be second-order in A. The rate constant for the reaction was determined to be 2.42 L/mol/s. If the initial concentration is 0.500 mol/L, what is the value of $t_{1/2}$?

Solution:

0.826 s

Exercise:

Problem:

The half-life of a reaction of compound *A* to give compounds *D* and *E* is 8.50 min when the initial concentration of *A* is 0.150 mol/L. How long will it take for the concentration to drop to 0.0300 mol/L if the reaction is (a) first order with respect to *A* or (b) second order with respect to *A*?

Exercise:**Problem:**

Some bacteria are resistant to the antibiotic penicillin because they produce penicillinase, an enzyme with a molecular weight of 3×10^4 g/mol that converts penicillin into inactive molecules. Although the kinetics of enzyme-catalyzed reactions can be complex, at low concentrations this reaction can be described by a rate equation that is first order in the catalyst (penicillinase) and that also involves the concentration of penicillin. From the following data: 1.0 L of a solution containing 0.15 μg (0.15×10^{-6} g) of penicillinase, determine the order of the reaction with respect to penicillin and the value of the rate constant.

[Penicillin] (M)	Rate (mol/L/min)
2.0×10^{-6}	1.0×10^{-10}
3.0×10^{-6}	1.5×10^{-10}
4.0×10^{-6}	2.0×10^{-10}

Solution:

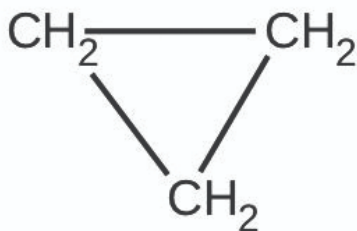
The reaction is first order.
 $k = 1.0 \times 10^7 \text{ L mol}^{-1} \text{ min}^{-1}$

Exercise:**Problem:**

Both technetium-99 and thallium-201 are used to image heart muscle in patients with suspected heart problems. The half-lives are 6 h and 73 h, respectively. What percent of the radioactivity would remain for each of the isotopes after 2 days (48 h)?

Exercise:**Problem:**

There are two molecules with the formula C_3H_6 . Propene, $\text{CH}_3\text{CH}=\text{CH}_2$, is the monomer of the polymer polypropylene, which is used for indoor-outdoor carpets. Cyclopropane is used as an anesthetic:



When heated to 499 °C, cyclopropane rearranges (isomerizes) and forms propene with a rate constant of $5.95 \times 10^{-4} \text{ s}^{-1}$. What is the half-life of this reaction? What fraction of the cyclopropane remains after 0.75 h at 499 °C?

Solution:

$1.67 \times 10^3 \text{ s}$; 20% remains

Exercise:

Problem:

Fluorine-18 is a radioactive isotope that decays by positron emission to form oxygen-18 with a half-life of 109.7 min. (A positron is a particle with the mass of an electron and a single unit of positive charge; the equation is ${}^{18}_{9}\text{F} \rightarrow {}^{18}_{8}\text{O} + {}^0_{+1}\text{e}$) Physicians use ${}^{18}\text{F}$ to study the brain by injecting a quantity of fluoro-substituted glucose into the blood of a patient. The glucose accumulates in the regions where the brain is active and needs nourishment.

- What is the rate constant for the decomposition of fluorine-18?
- If a sample of glucose containing radioactive fluorine-18 is injected into the blood, what percent of the radioactivity will remain after 5.59 h?
- How long does it take for 99.99% of the ${}^{18}\text{F}$ to decay?

Exercise:

Problem:

Suppose that the half-life of steroids taken by an athlete is 42 days. Assuming that the steroids biodegrade by a first-order process, how long would it take for $\frac{1}{64}$ of the initial dose to remain in the athlete's body?

Solution:

252 days

Exercise:

Problem:

Recently, the skeleton of King Richard III was found under a parking lot in England. If tissue samples from the skeleton contain about 93.79% of the carbon-14 expected in living tissue, what year did King Richard III die? The half-life for carbon-14 is 5730 years.

Exercise:

Problem:

Nitroglycerine is an extremely sensitive explosive. In a series of carefully controlled experiments, samples of the explosive were heated to 160 °C and their first-order decomposition studied. Determine the average rate constants for each experiment using the following data:

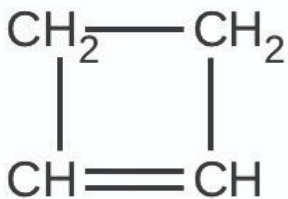
Initial [C ₃ H ₅ N ₃ O ₉] (M)	4.88	3.52	2.29	1.81	5.33	4.05	2.95	1.72
<i>t</i> (s)	300	300	300	300	180	180	180	180
% Decomposed	52.0	52.9	53.2	53.9	34.6	35.9	36.0	35.4

Solution:

[A] ₀ (M)	<i>k</i> × 10 ³ (s ⁻¹)
4.88	2.45
3.52	2.51
2.29	2.53
1.81	2.58
5.33	2.36
4.05	2.47
2.95	2.48
1.72	2.43

Exercise:**Problem:**

For the past 10 years, the unsaturated hydrocarbon 1,3-butadiene (CH₂ = CH–CH = CH₂) has ranked 38th among the top 50 industrial chemicals. It is used primarily for the manufacture of synthetic rubber. An isomer exists also as cyclobutene:



The isomerization of cyclobutene to butadiene is first-order and the rate constant has been measured as $2.0 \times 10^{-4} \text{ s}^{-1}$ at 150°C in a 0.53-L flask. Determine the partial pressure of cyclobutene and its concentration after 30.0 minutes if an isomerization reaction is carried out at 150°C with an initial pressure of 55 torr.

Glossary

half-life of a reaction ($t_{1/2}$)

time required for half of a given amount of reactant to be consumed

integrated rate law

equation that relates the concentration of a reactant to elapsed time of reaction

Collision Theory

By the end of this section, you will be able to:

- Use the postulates of collision theory to explain the effects of physical state, temperature, and concentration on reaction rates
- Define the concepts of activation energy and transition state
- Use the Arrhenius equation in calculations relating rate constants to temperature

We should not be surprised that atoms, molecules, or ions must collide before they can react with each other. Atoms must be close together to form chemical bonds. This simple premise is the basis for a very powerful theory that explains many observations regarding chemical kinetics, including factors affecting reaction rates.

Collision theory is based on the following postulates:

1. The rate of a reaction is proportional to the rate of reactant collisions:

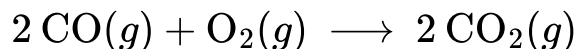
Equation:

$$\text{reaction rate} \propto \frac{\# \text{ collisions}}{\text{time}}$$

2. The reacting species must collide in an orientation that allows contact between the atoms that will become bonded together in the product.
3. The collision must occur with adequate energy to permit mutual penetration of the reacting species' valence shells so that the electrons can rearrange and form new bonds (and new chemical species).

We can see the importance of the two physical factors noted in postulates 2 and 3, the orientation and energy of collisions, when we consider the reaction of carbon monoxide with oxygen:

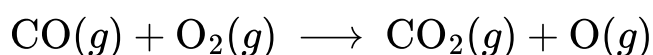
Equation:



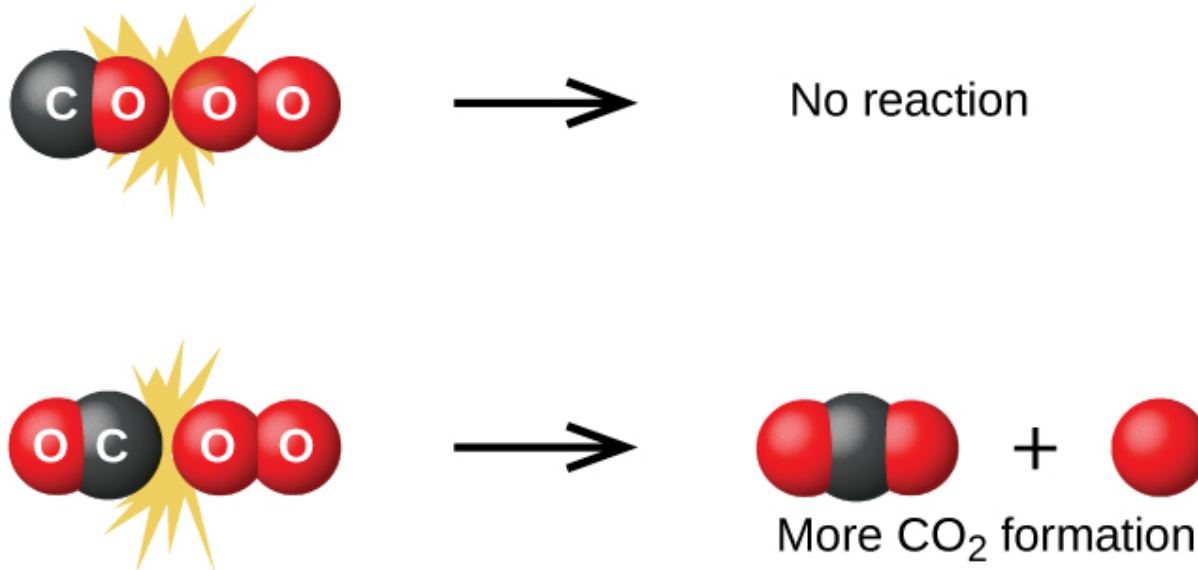
Carbon monoxide is a pollutant produced by the combustion of hydrocarbon fuels. To reduce this pollutant, automobiles have catalytic converters that use a catalyst to carry out this reaction. It is also a side reaction of the combustion of gunpowder that results in muzzle flash for many firearms. If carbon monoxide and oxygen are present in sufficient quantity, the reaction is spontaneous at high temperature and pressure.

The first step in the gas-phase reaction between carbon monoxide and oxygen is a collision between the two molecules:

Equation:



Although there are many different possible orientations the two molecules can have relative to each other, consider the two presented in [\[link\]](#). In the first case, the oxygen side of the carbon monoxide molecule collides with the oxygen molecule. In the second case, the carbon side of the carbon monoxide molecule collides with the oxygen molecule. The second case is clearly more likely to result in the formation of carbon dioxide, which has a central carbon atom bonded to two oxygen atoms ($\text{O} = \text{C} = \text{O}$). This is a rather simple example of how important the orientation of the collision is in terms of creating the desired product of the reaction.



Illustrated are two collisions that might take place between carbon

monoxide and oxygen molecules. The orientation of the colliding molecules partially determines whether a reaction between the two molecules will occur.

If the collision does take place with the correct orientation, there is still no guarantee that the reaction will proceed to form carbon dioxide. In addition to a proper orientation, the collision must also occur with sufficient energy to result in product formation. When reactant species collide with both proper orientation and adequate energy, they combine to form an unstable species called an **activated complex** or a **transition state**. As an example, [\[link\]](#) depicts the structure of possible transition states in the reaction between CO and O₂ to form CO₂.



Possible transition states (activated complexes) for carbon monoxide reacting with oxygen to form carbon dioxide.

Solid lines represent covalent bonds, while dotted lines represent unstable orbital overlaps that may, or may not, become covalent bonds as

product is formed.

In the first two examples in this figure, the O=O double bond is not impacted; therefore, carbon dioxide cannot form. The third proposed transition state will result in the formation of carbon dioxide if the third “extra” oxygen atom separates from the rest of the molecule.

In most circumstances, it is impossible to isolate or identify a transition state or activated complex. In the reaction between carbon monoxide and oxygen to form carbon dioxide, activated complexes have only been observed spectroscopically in systems that utilize a heterogeneous catalyst. The gas-phase reaction occurs too rapidly to isolate any such chemical compound.

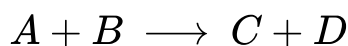
Collision theory explains why most reaction rates increase as concentrations increase. With an increase in the concentration of any reacting substance, the chances for collisions between molecules are increased because there are more molecules per unit of volume. More collisions mean a faster reaction rate, assuming the energy of the collisions is adequate.

Activation Energy and the Arrhenius Equation

The minimum energy necessary to form a product during a collision between reactants is called the **activation energy (E_a)**. The kinetic energy of reactant molecules plays an important role in a reaction because the energy necessary to form a product is provided by a collision of a reactant molecule with another reactant molecule. (In single-reactant reactions, activation energy may be provided by a collision of the reactant molecule with the wall of the reaction vessel or with molecules of an inert contaminant.) If the activation energy is much larger than the average kinetic energy of the molecules, the reaction will occur slowly: Only a few fast-moving molecules will have enough energy to react. If the activation energy is much smaller than the average kinetic energy of the molecules, the fraction of molecules possessing the necessary kinetic energy will be large; most collisions between molecules will result in reaction, and the reaction will occur rapidly.

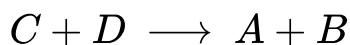
[\[link\]](#) shows the energy relationships for the general reaction of a molecule of A with a molecule of B to form molecules of C and D :

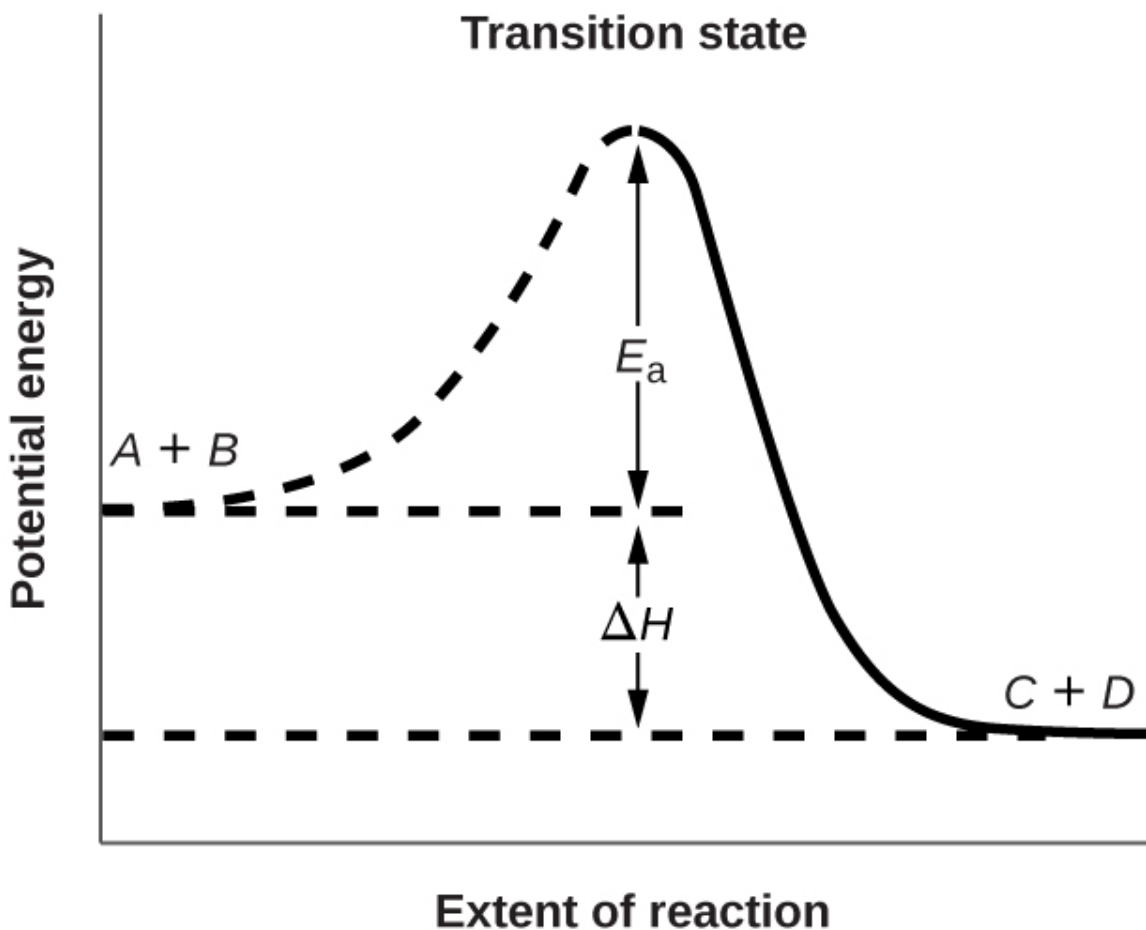
Equation:



The figure shows that the energy of the transition state is higher than that of the reactants A and B by an amount equal to E_a , the activation energy. Thus, the sum of the kinetic energies of A and B must be equal to or greater than E_a to reach the transition state. After the transition state has been reached, and as C and D begin to form, the system loses energy until its total energy is lower than that of the initial mixture. This lost energy is transferred to other molecules, giving them enough energy to reach the transition state. The forward reaction (that between molecules A and B) therefore tends to take place readily once the reaction has started. In [\[link\]](#), ΔH represents the difference in enthalpy between the reactants (A and B) and the products (C and D). The sum of E_a and ΔH represents the activation energy for the reverse reaction:

Equation:





This graph shows the potential energy relationships for the reaction $A + B \rightarrow C + D$. The dashed portion of the curve represents the energy of the system with a molecule of A and a molecule of B present, and the solid portion represents the energy of the system with a molecule of C and a molecule of D present. The activation energy for the forward reaction is represented by E_a . The activation energy for the reverse reaction is greater than that for the forward reaction by an amount equal to ΔH . The curve's peak represents the transition state.

We can use the **Arrhenius equation** to relate the activation energy and the rate constant, k , of a given reaction:

Equation:

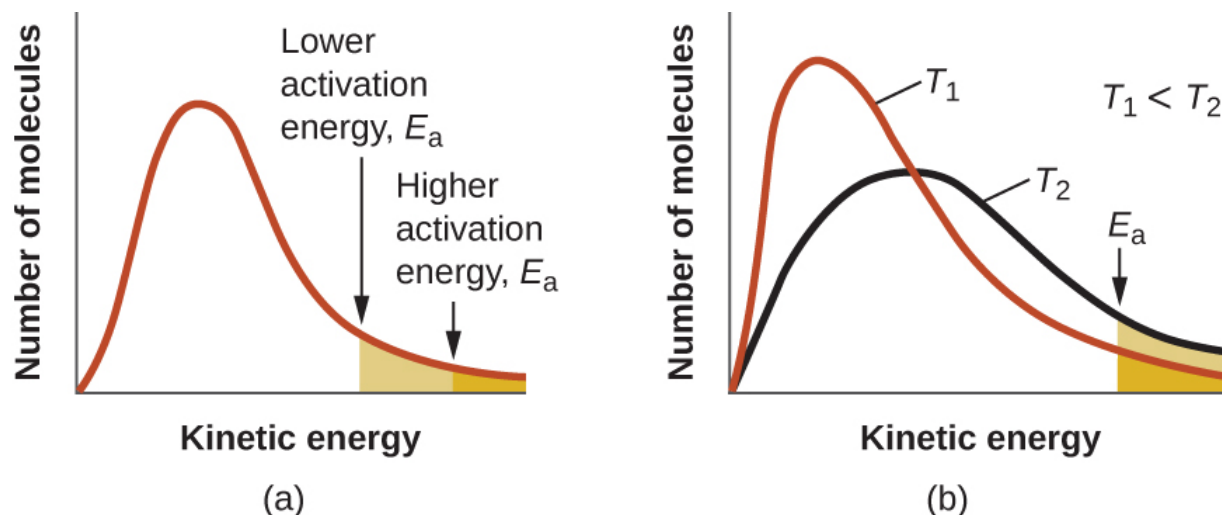
$$k = Ae^{-E_a/RT}$$

In this equation, R is the ideal gas constant, which has a value 8.314 J/mol/K, T is temperature on the Kelvin scale, E_a is the activation energy in joules per mole, e is the constant 2.7183, and A is a constant called the **frequency factor**, which is related to the frequency of collisions and the orientation of the reacting molecules.

The postulates of collision theory are accommodated in the Arrhenius equation. The frequency factor A is related to the rate at which collisions having the correct *orientation* occur. The exponential term, $e^{-E_a/RT}$, is related to the fraction of collisions providing adequate *energy* to overcome the activation barrier of the reaction.

At one extreme, the system does not contain enough energy for collisions to overcome the activation barrier. In such cases, no reaction occurs. At the other extreme, the system has so much energy that every collision with the correct orientation can overcome the activation barrier, causing the reaction to proceed. In such cases, the reaction is nearly instantaneous.

The Arrhenius equation describes quantitatively much of what we have already discussed about reaction rates. For two reactions at the same temperature, the reaction with the higher activation energy has the lower rate constant and the slower rate. The larger value of E_a results in a smaller value for $e^{-E_a/RT}$, reflecting the smaller fraction of molecules with enough energy to react. Alternatively, the reaction with the smaller E_a has a larger fraction of molecules with enough energy to react. This will be reflected as a larger value of $e^{-E_a/RT}$, a larger rate constant, and a faster rate for the reaction. An increase in temperature has the same effect as a decrease in activation energy. A larger fraction of molecules has the necessary energy to react ([\[link\]](#)), as indicated by an increase in the value of $e^{-E_a/RT}$. The rate constant is also directly proportional to the frequency factor, A . Hence a change in conditions or reactants that increases the number of collisions with a favorable orientation for reaction results in an increase in A and, consequently, an increase in k .



(a) As the activation energy of a reaction decreases, the number of molecules with at least this much energy increases, as shown by the shaded areas. (b) At a higher temperature, T_2 , more molecules have kinetic energies greater than E_a , as shown by the yellow shaded area.

A convenient approach for determining E_a for a reaction involves the measurement of k at different temperatures and using an alternate version of the Arrhenius equation that takes the form of a linear equation

Equation:

$$\ln k = \left(\frac{-E_a}{R} \right) \left(\frac{1}{T} \right) + \ln A$$

$$y = mx + b$$

Thus, a plot of $\ln k$ versus $\frac{1}{T}$ gives a straight line with the slope $\frac{-E_a}{R}$, from which E_a may be determined. The intercept gives the value of $\ln A$.

Example:

Determination of E_a

The variation of the rate constant with temperature for the decomposition of HI(*g*) to H₂(*g*) and I₂(*g*) is given here. What is the activation energy for the reaction?

Equation:



<i>T</i> (K)	<i>k</i> (L/mol/s)
555	3.52×10^{-7}
575	1.22×10^{-6}
645	8.59×10^{-5}
700	1.16×10^{-3}
781	3.95×10^{-2}

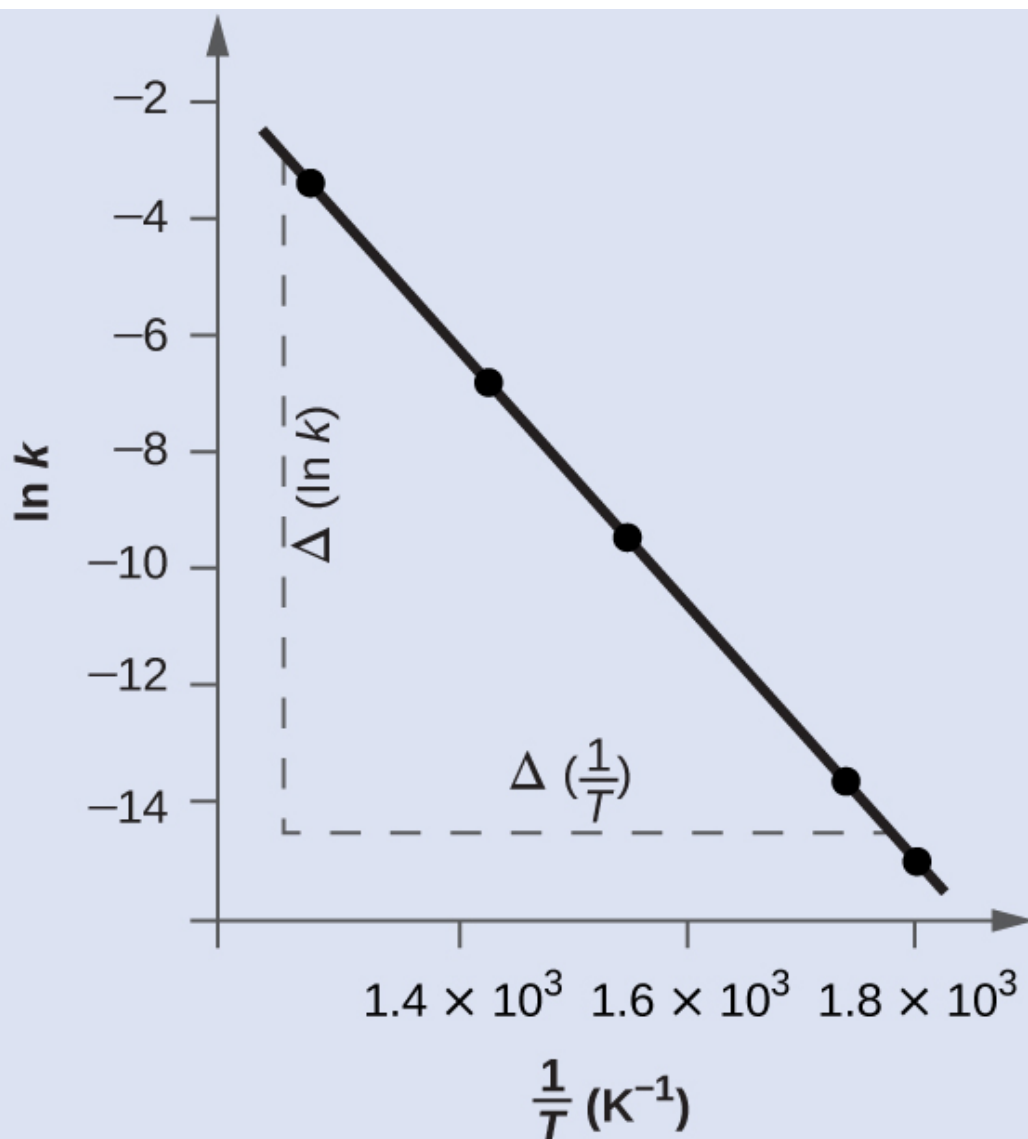
Solution

Values of $\frac{1}{T}$ and $\ln k$ are:

$\frac{1}{T}$ (K ⁻¹)	$\ln k$
1.80×10^{-3}	-14.860

$\frac{1}{T}$ (K ⁻¹)	ln <i>k</i>
1.74×10^{-3}	-13.617
1.55×10^{-3}	-9.362
1.43×10^{-3}	-6.759
1.28×10^{-3}	-3.231

[\[link\]](#) is a graph of ln *k* versus $\frac{1}{T}$. To determine the slope of the line, we need two values of ln *k*, which are determined from the line at two values of $\frac{1}{T}$ (one near each end of the line is preferable). For example, the value of ln *k* determined from the line when $\frac{1}{T} = 1.25 \times 10^{-3}$ is -2.593; the value when $\frac{1}{T} = 1.78 \times 10^{-3}$ is -14.447.



This graph shows the linear relationship between $\ln k$ and $\frac{1}{T}$ for the reaction $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$ according to the Arrhenius equation.

The slope of this line is given by the following expression:

Equation:

$$\begin{aligned}
 \text{Slope} &= \frac{\Delta(\ln k)}{\Delta\left(\frac{1}{T}\right)} \\
 &= \frac{(-14.447) - (-2.593)}{(1.78 \times 10^{-3} \text{ K}^{-1}) - (1.25 \times 10^{-3} \text{ K}^{-1})} \\
 &= \frac{-11.854}{0.53 \times 10^{-3} \text{ K}^{-1}} = 2.2 \times 10^4 \text{ K} \\
 &= -\frac{E_a}{R}
 \end{aligned}$$

Thus:

Equation:

$$E_a = -\text{slope} \times R = -(-2.2 \times 10^4 \text{ K} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1})$$

Equation:

$$E_a = 1.8 \times 10^5 \text{ J mol}^{-1}$$

In many situations, it is possible to obtain a reasonable estimate of the activation energy without going through the entire process of constructing the Arrhenius plot. The Arrhenius equation:

Equation:

$$\ln k = \left(\frac{-E_a}{R} \right) \left(\frac{1}{T} \right) + \ln A$$

can be rearranged as shown to give:

Equation:

$$\frac{\Delta(\ln k)}{\Delta\left(\frac{1}{T}\right)} = -\frac{E_a}{R}$$

or

Equation:

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

This equation can be rearranged to give a one-step calculation to obtain an estimate for the activation energy:

Equation:

$$E_a = -R \left(\frac{\ln k_2 - \ln k_1}{\left(\frac{1}{T_2}\right) - \left(\frac{1}{T_1}\right)} \right)$$

Using the experimental data presented here, we can simply select two data entries. For this example, we select the first entry and the last entry:

<i>T</i> (K)	<i>k</i> (L/mol/s)	$\frac{1}{T}$ (K ⁻¹)	ln <i>k</i>
555	3.52×10^{-7}	1.80×10^{-3}	-14.860
781	3.95×10^{-2}	1.28×10^{-3}	-3.231

After calculating $\frac{1}{T}$ and ln *k*, we can substitute into the equation:

Equation:

$$E_a = -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \left(\frac{-3.231 - (-14.860)}{1.28 \times 10^{-3} \text{ K}^{-1} - 1.80 \times 10^{-3} \text{ K}^{-1}} \right)$$

and the result is $E_a = 185,900 \text{ J/mol}$.

This method is very effective, especially when a limited number of temperature-dependent rate constants are available for the reaction of interest.

Check Your Learning

The rate constant for the rate of decomposition of N₂O₅ to NO and O₂ in the gas phase is 1.66 L/mol/s at 650 K and 7.39 L/mol/s at 700 K:

Equation:



Assuming the kinetics of this reaction are consistent with the Arrhenius equation, calculate the activation energy for this decomposition.

Note:

Answer:

113,000 J/mol

Key Concepts and Summary

Chemical reactions require collisions between reactant species. These reactant collisions must be of proper orientation and sufficient energy in order to result in product formation. Collision theory provides a simple but effective explanation for the effect of many experimental parameters on reaction rates. The Arrhenius equation describes the relation between a reaction's rate constant and its activation energy, temperature, and dependence on collision orientation.

Key Equations

- $k = Ae^{-E_a/RT}$
- $\ln k = \left(\frac{-E_a}{R} \right) \left(\frac{1}{T} \right) + \ln A$
- $\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$

Chemistry End of Chapter Exercises

Exercise:

Problem:

Chemical reactions occur when reactants collide. What are two factors that may prevent a collision from producing a chemical reaction?

Solution:

The reactants either may be moving too slowly to have enough kinetic energy to exceed the activation energy for the reaction, or the orientation of the molecules when they collide may prevent the reaction from occurring.

Exercise:**Problem:**

When every collision between reactants leads to a reaction, what determines the rate at which the reaction occurs?

Exercise:**Problem:**

What is the activation energy of a reaction, and how is this energy related to the activated complex of the reaction?

Solution:

The activation energy is the minimum amount of energy necessary to form the activated complex in a reaction. It is usually expressed as the energy necessary to form one mole of activated complex.

Exercise:**Problem:**

Account for the relationship between the rate of a reaction and its activation energy.

Exercise:

Problem:

Describe how graphical methods can be used to determine the activation energy of a reaction from a series of data that includes the rate of reaction at varying temperatures.

Solution:

After finding k at several different temperatures, a plot of $\ln k$ versus $\frac{1}{T}$, gives a straight line with the slope $\frac{-E_a}{R}$ from which E_a may be determined.

Exercise:**Problem:**

How does an increase in temperature affect rate of reaction? Explain this effect in terms of the collision theory of the reaction rate.

Exercise:**Problem:**

The rate of a certain reaction doubles for every 10 °C rise in temperature.

- (a) How much faster does the reaction proceed at 45 °C than at 25 °C?
 - (b) How much faster does the reaction proceed at 95 °C than at 25 °C?
-

Solution:

- (a) 4-times faster (b) 128-times faster

Exercise:

Problem:

In an experiment, a sample of NaClO_3 was 90% decomposed in 48 min. Approximately how long would this decomposition have taken if the sample had been heated 20°C higher? (Hint: Assume the rate doubles for each 10°C rise in temperature.)

Exercise:**Problem:**

The rate constant at 325°C for the decomposition reaction $\text{C}_4\text{H}_8 \longrightarrow 2\text{C}_2\text{H}_4$ is $6.1 \times 10^{-8} \text{ s}^{-1}$, and the activation energy is 261 kJ per mole of C_4H_8 . Determine the frequency factor for the reaction.

Solution:

$$3.9 \times 10^{15} \text{ s}^{-1}$$

Exercise:**Problem:**

The rate constant for the decomposition of acetaldehyde, CH_3CHO , to methane, CH_4 , and carbon monoxide, CO , in the gas phase is $1.1 \times 10^{-2} \text{ L/mol/s}$ at 703 K and 4.95 L/mol/s at 865 K. Determine the activation energy for this decomposition.

Exercise:

Problem:

An elevated level of the enzyme alkaline phosphatase (ALP) in human serum is an indication of possible liver or bone disorder. The level of serum ALP is so low that it is very difficult to measure directly. However, ALP catalyzes a number of reactions, and its relative concentration can be determined by measuring the rate of one of these reactions under controlled conditions. One such reaction is the conversion of p-nitrophenyl phosphate (PNPP) to p-nitrophenoxide ion (PNP) and phosphate ion. Control of temperature during the test is very important; the rate of the reaction increases 1.47 times if the temperature changes from 30 °C to 37 °C. What is the activation energy for the ALP-catalyzed conversion of PNPP to PNP and phosphate?

Solution:

43.0 kJ/mol

Exercise:**Problem:**

In terms of collision theory, to which of the following is the rate of a chemical reaction proportional?

- (a) the change in free energy per second
- (b) the change in temperature per second
- (c) the number of collisions per second
- (d) the number of product molecules

Exercise:

Problem:

Hydrogen iodide, HI, decomposes in the gas phase to produce hydrogen, H₂, and iodine, I₂. The value of the rate constant, k , for the reaction was measured at several different temperatures and the data are shown here:

Temperature (K)	k ($M^{-1} s^{-1}$)
555	6.23×10^{-7}
575	2.42×10^{-6}
645	1.44×10^{-4}
700	2.01×10^{-3}

What is the value of the activation energy (in kJ/mol) for this reaction?

Solution:

177 kJ/mol

Exercise:**Problem:**

The element Co exists in two oxidation states, Co(II) and Co(III), and the ions form many complexes. The rate at which one of the complexes of Co(III) was reduced by Fe(II) in water was measured. Determine the activation energy of the reaction from the following data:

T (K)	k (s ⁻¹)
293	0.054
298	0.100

Exercise:

Problem:

The hydrolysis of the sugar sucrose to the sugars glucose and fructose,
 $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \longrightarrow \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$

follows a first-order rate equation for the disappearance of sucrose:
 Rate = $k[\text{C}_{12}\text{H}_{22}\text{O}_{11}]$ (The products of the reaction, glucose and fructose, have the same molecular formulas but differ in the arrangement of the atoms in their molecules.)

(a) In neutral solution, $k = 2.1 \times 10^{-11} \text{ s}^{-1}$ at 27 °C and $8.5 \times 10^{-11} \text{ s}^{-1}$ at 37 °C. Determine the activation energy, the frequency factor, and the rate constant for this equation at 47 °C (assuming the kinetics remain consistent with the Arrhenius equation at this temperature).

(b) When a solution of sucrose with an initial concentration of 0.150 M reaches equilibrium, the concentration of sucrose is $1.65 \times 10^{-7} M$. How long will it take the solution to reach equilibrium at 27 °C in the absence of a catalyst? Because the concentration of sucrose at equilibrium is so low, assume that the reaction is irreversible.

(c) Why does assuming that the reaction is irreversible simplify the calculation in part (b)?

Solution:

$$E_a = 108 \text{ kJ}$$

$$A = 2.0 \times 10^8 \text{ s}^{-1}$$

$$k = 3.2 \times 10^{-10} \text{ s}^{-1}$$

(b) 1.81×10^8 h or 7.6×10^6 day. (c) Assuming that the reaction is irreversible simplifies the calculation because we do not have to account for any reactant that, having been converted to product, returns to the original state.

Exercise:

Problem:

Use the [PhET Reactions & Rates interactive simulation](#) to simulate a system. On the “Single collision” tab of the simulation applet, enable the “Energy view” by clicking the “+” icon. Select the first $A + BC \longrightarrow AB + C$ reaction (A is yellow, B is purple, and C is navy blue). Using the “straight shot” default option, try launching the A atom with varying amounts of energy. What changes when the Total Energy line at launch is below the transition state of the Potential Energy line? Why? What happens when it is above the transition state? Why?

Exercise:

Problem:

Use the [PhET Reactions & Rates interactive simulation](#) to simulate a system. On the “Single collision” tab of the simulation applet, enable the “Energy view” by clicking the “+” icon. Select the first $A + BC \longrightarrow AB + C$ reaction (A is yellow, B is purple, and C is navy blue). Using the “angled shot” option, try launching the A atom with varying angles, but with more Total energy than the transition state. What happens when the A atom hits the BC molecule from different directions? Why?

Solution:

The A atom has enough energy to react with BC; however, the different angles at which it bounces off of BC without reacting indicate that the orientation of the molecule is an important part of the reaction kinetics and determines whether a reaction will occur.

Glossary

activated complex

(also, transition state) unstable combination of reactant species representing the highest energy state of a reaction system

activation energy (E_a)

energy necessary in order for a reaction to take place

Arrhenius equation

mathematical relationship between the rate constant and the activation energy of a reaction

collision theory

model that emphasizes the energy and orientation of molecular collisions to explain and predict reaction kinetics

frequency factor (A)

proportionality constant in the Arrhenius equation, related to the relative number of collisions having an orientation capable of leading to product formation

Reaction Mechanisms

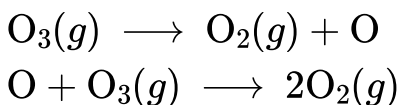
By the end of this section, you will be able to:

- Distinguish net reactions from elementary reactions (steps)
- Identify the molecularity of elementary reactions
- Write a balanced chemical equation for a process given its reaction mechanism
- Derive the rate law consistent with a given reaction mechanism

A balanced equation for a chemical reaction indicates what is reacting and what is produced, but it reveals nothing about how the reaction actually takes place. The **reaction mechanism** (or reaction path) is the process, or pathway, by which a reaction occurs.

A chemical reaction usually occurs in steps, although it may not always be obvious to an observer. The decomposition of ozone, for example, appears to follow a mechanism with two steps:

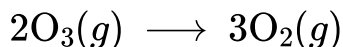
Equation:



We call each step in a reaction mechanism an **elementary reaction**.

Elementary reactions occur exactly as they are written and cannot be broken down into simpler steps. Elementary reactions add up to the overall reaction, which, for the decomposition, is:

Equation:



Notice that the oxygen atom produced in the first step of this mechanism is consumed in the second step and therefore does not appear as a product in the overall reaction. Species that are produced in one step and consumed in a subsequent step are called **intermediates**.

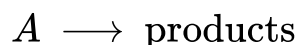
While the overall reaction equation for the decomposition of ozone indicates that two molecules of ozone react to give three molecules of oxygen, the mechanism of the reaction does not involve the collision and reaction of two

ozone molecules. Rather, it involves a molecule of ozone decomposing to an oxygen molecule and an intermediate oxygen atom; the oxygen atom then reacts with a second ozone molecule to give two oxygen molecules. These two elementary reactions occur exactly as they are shown in the reaction mechanism.

Unimolecular Elementary Reactions

The **molecularity** of an elementary reaction is the number of reactant species (atoms, molecules, or ions). For example, a **unimolecular reaction** involves the rearrangement of a *single* reactant species to produce one or more molecules of product:

Equation:



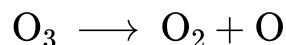
The rate equation for a unimolecular reaction is:

Equation:

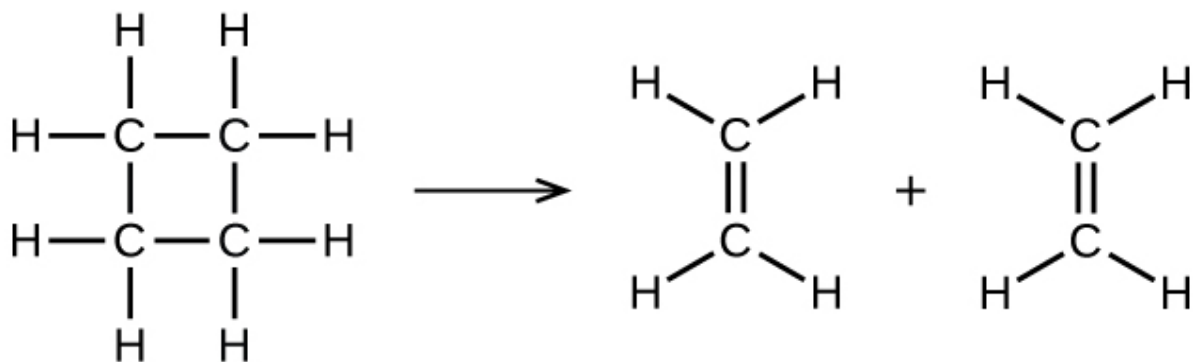
$$\text{rate} = k[A]$$

A unimolecular reaction may be one of several elementary reactions in a complex mechanism. For example, the reaction:

Equation:

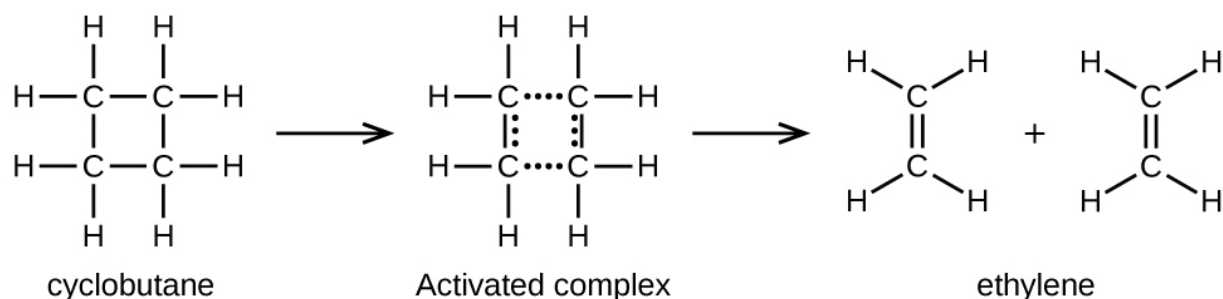


illustrates a unimolecular elementary reaction that occurs as one part of a two-step reaction mechanism. However, some unimolecular reactions may have only a single reaction in the reaction mechanism. (In other words, an elementary reaction can also be an overall reaction in some cases.) For example, the gas-phase decomposition of cyclobutane, C_4H_8 , to ethylene, C_2H_4 , occurs via a unimolecular, single-step mechanism:



For these unimolecular reactions to occur, all that is required is the separation of parts of single reactant molecules into products.

Chemical bonds do not simply fall apart during chemical reactions. Energy is required to break chemical bonds. The activation energy for the decomposition of C_4H_8 , for example, is 261 kJ per mole. This means that it requires 261 kilojoules to distort one mole of these molecules into activated complexes that decompose into products:



In a sample of C_4H_8 , a few of the rapidly moving C_4H_8 molecules collide with other rapidly moving molecules and pick up additional energy. When the C_4H_8 molecules gain enough energy, they can transform into an activated complex, and the formation of ethylene molecules can occur. In effect, a particularly energetic collision knocks a C_4H_8 molecule into the geometry of the activated complex. However, only a small fraction of gas molecules travel at sufficiently high speeds with large enough kinetic energies to accomplish this. Hence, at any given moment, only a few molecules pick up enough energy from collisions to react.

The rate of decomposition of C_4H_8 is directly proportional to its concentration. Doubling the concentration of C_4H_8 in a sample gives twice as many

molecules per liter. Although the fraction of molecules with enough energy to react remains the same, the total number of such molecules is twice as great. Consequently, there is twice as much C_4H_8 per liter, and the reaction rate is twice as fast:

Equation:

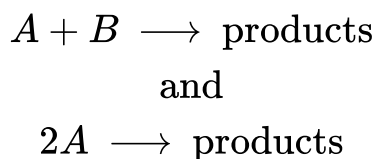
$$\text{rate} = - \frac{\Delta[\text{C}_4\text{H}_8]}{\Delta t} = k[\text{C}_4\text{H}_8]$$

A similar relationship applies to any unimolecular elementary reaction; the reaction rate is directly proportional to the concentration of the reactant, and the reaction exhibits first-order behavior. The proportionality constant is the rate constant for the particular unimolecular reaction.

Bimolecular Elementary Reactions

The collision and combination of two molecules or atoms to form an activated complex in an elementary reaction is called a **bimolecular reaction**. There are two types of bimolecular elementary reactions:

Equation:



For the first type, in which the two reactant molecules are different, the rate law is first-order in A and first order in B :

Equation:

$$\text{rate} = k[A][B]$$

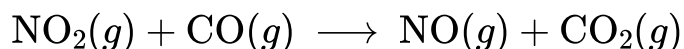
For the second type, in which two identical molecules collide and react, the rate law is second order in A :

Equation:

$$\text{rate} = k[A][A] = k[A]^2$$

Some chemical reactions have mechanisms that consist of a single bimolecular elementary reaction. One example is the reaction of nitrogen dioxide with carbon monoxide:

Equation:



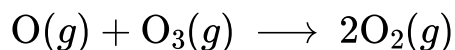
(see [\[link\]](#))



The probable mechanism for the reaction between NO₂ and CO to yield NO and CO₂.

Bimolecular elementary reactions may also be involved as steps in a multistep reaction mechanism. The reaction of atomic oxygen with ozone is one example:

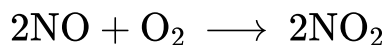
Equation:



Termolecular Elementary Reactions

An elementary **termolecular reaction** involves the simultaneous collision of three atoms, molecules, or ions. Termolecular elementary reactions are uncommon because the probability of three particles colliding simultaneously is less than one one-thousandth of the probability of two particles colliding. There are, however, a few established termolecular elementary reactions. The reaction of nitric oxide with oxygen appears to involve termolecular steps:

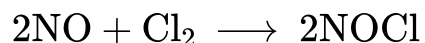
Equation:



$$\text{rate} = k[\text{NO}]^2[\text{O}_2]$$

Likewise, the reaction of nitric oxide with chlorine appears to involve termolecular steps:

Equation:



$$\text{rate} = k[\text{NO}]^2[\text{Cl}_2]$$

Relating Reaction Mechanisms to Rate Laws

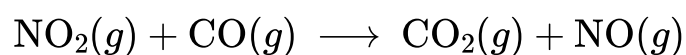
It's often the case that one step in a multistep reaction mechanism is significantly slower than the others. Because a reaction cannot proceed faster than its slowest step, this step will limit the rate at which the overall reaction occurs. The slowest step is therefore called the **rate-limiting step** (or rate-determining step) of the reaction [\[link\]](#).



A cattle chute is a nonchemical example of a rate-determining step. Cattle can only be moved from one holding pen to another as quickly as one animal can make its way through the chute. (credit: Loren Kerns)

As described earlier, rate laws may be derived directly from the chemical equations for elementary reactions. This is not the case, however, for ordinary chemical reactions. The balanced equations most often encountered represent the overall change for some chemical system, and very often this is the result of some multistep reaction mechanisms. In every case, we must determine the overall rate law from experimental data and deduce the mechanism from the rate law (and sometimes from other data). The reaction of NO_2 and CO provides an illustrative example:

Equation:



For temperatures above 225 °C, the rate law has been found to be:

Equation:

$$\text{rate} = k [\text{NO}_2] [\text{CO}]$$

The reaction is first order with respect to NO₂ and first-order with respect to CO. This is consistent with a single-step bimolecular mechanism and it is *possible* that this is the mechanism for this reaction at high temperatures.

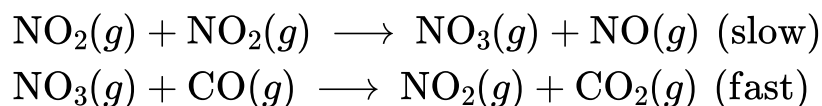
At temperatures below 225 °C, the reaction is described by a rate law that is second order with respect to NO₂:

Equation:

$$\text{rate} = k[\text{NO}_2]^2$$

This is consistent with a mechanism that involves the following two elementary reactions, the first of which is slower and is therefore the rate-determining step:

Equation:



The rate-determining step gives a rate law showing second-order dependence on the NO₂ concentration, and the sum of the two equations gives the net overall reaction.

In general, when the rate-determining (slower) step is the first step in a mechanism, the rate law for the overall reaction is the same as the rate law for this step. However, when the rate-determining step is preceded by a step involving an *equilibrium* reaction, the rate law for the overall reaction may be more difficult to derive.

An elementary reaction is at equilibrium when it proceeds in both the forward and reverse directions at equal rates. Consider the dimerization of NO to N₂O₂, with k_1 used to represent the rate constant of the forward reaction and k_{-1} used to represent the rate constant of the reverse reaction:

Equation:

$$\text{rate}_{\text{forward}} = \text{rate}_{\text{reverse}}$$

$$k_1[\text{NO}]^2 = k_{-1}[\text{N}_2\text{O}_2]$$

If N_2O_2 was an intermediate in a mechanism, this expression could be rearranged to represent the concentration of N_2O_2 in the overall rate law expression using algebraic manipulation:

Equation:

$$\left(\frac{k_1[\text{NO}]^2}{k_{-1}} \right) = [\text{N}_2\text{O}_2]$$

However, once again, intermediates cannot be listed as part of the overall rate law expression, though they can be included in an individual elementary reaction of a mechanism. [\[link\]](#) will illustrate how to derive overall rate laws from mechanisms involving equilibrium steps preceding the rate-determining step.

Example:**Deriving the Overall Rate Law Expression for a Multistep Reaction Mechanism**

Nitryl chloride (NO_2Cl) decomposes to nitrogen dioxide (NO_2) and chlorine gas (Cl_2) according to the following mechanism:

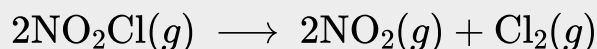
1. $2\text{NO}_2\text{Cl}(g) \rightleftharpoons \text{ClO}_2(g) + \text{N}_2\text{O}(g) + \text{ClO}(g)$ (fast, k_1 represents the rate constant for the forward reaction and k_{-1} the rate constant for the reverse reaction)
2. $\text{N}_2\text{O}(g) + \text{ClO}_2(g) \rightleftharpoons \text{NO}_2(g) + \text{NOCl}(g)$ (fast, k_2 for the forward reaction, k_{-2} for the reverse reaction)
3. $\text{NOCl} + \text{ClO} \longrightarrow \text{NO}_2 + \text{Cl}_2$ (slow, k_3 the rate constant for the forward reaction)

Determine the overall reaction, write the rate law expression for each elementary reaction, identify any intermediates, and determine the overall rate law expression.

Solution

For the overall reaction, simply sum the three steps, cancel intermediates, and combine like formulas:

Equation:



Next, write the rate law expression for each elementary reaction. Remember that for elementary reactions that are part of a mechanism, the rate law expression can be derived directly from the stoichiometry:

Equation:

$$\begin{aligned}k_1[\text{NO}_2\text{Cl}]_2 &= k_{-1}[\text{ClO}_2][\text{N}_2\text{O}][\text{ClO}] \\k_2[\text{N}_2\text{O}][\text{ClO}_2] &= k_{-2}[\text{NO}_2][\text{NOCl}] \\ \text{Rate} &= k_3[\text{NOCl}][\text{ClO}]\end{aligned}$$

The third step, which is the slow step, is the rate-determining step. Therefore, the overall rate law expression could be written as $\text{Rate} = k_3[\text{NOCl}][\text{ClO}]$. However, both NOCl and ClO are intermediates. Algebraic expressions must be used to represent $[\text{NOCl}]$ and $[\text{ClO}]$ such that no intermediates remain in the overall rate law expression.

Using elementary reaction 1, $[\text{ClO}] = \frac{k_1[\text{NO}_2\text{Cl}]^2}{k_{-1}[\text{ClO}_2][\text{N}_2\text{O}]}$.

Using elementary reaction 2, $[\text{NOCl}] = \frac{k_2[\text{N}_2\text{O}][\text{ClO}_2]}{k_{-2}[\text{NO}_2]}$.

Now substitute these algebraic expressions into the overall rate law expression and simplify:

Equation:

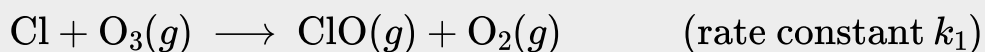
$$\begin{aligned}\text{rate} &= k_3 \left(\frac{k_2[\text{N}_2\text{O}][\text{ClO}_2]}{k_{-2}[\text{NO}_2]} \right) \left(\frac{k_1[\text{NO}_2\text{Cl}]^2}{k_{-1}[\text{ClO}_2][\text{N}_2\text{O}]} \right) \\ \text{rate} &= \frac{k_3 k_2 k_1 [\text{NO}_2\text{Cl}]^2}{k_{-2} k_{-1} [\text{NO}_2]}\end{aligned}$$

Notice that this rate law shows an *inverse* dependence on the concentration of one of the product species, consistent with the presence of an equilibrium step in the reaction mechanism.

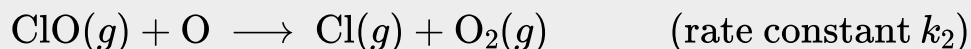
Check Your Learning

Atomic chlorine in the atmosphere reacts with ozone in the following pair of elementary reactions:

Equation:



Equation:



Determine the overall reaction, write the rate law expression for each elementary reaction, identify any intermediates, and determine the overall rate law expression.

Note:

Answer:

overall reaction: $\text{O}_3(g) + \text{O} \longrightarrow 2\text{O}_2(g)$

rate₁ = $k_1[\text{O}_3][\text{Cl}]$; rate₂ = $k_2[\text{ClO}][\text{O}]$

intermediate: $\text{ClO}(g)$

overall rate = $k_2k_1[\text{O}_3][\text{Cl}][\text{O}]$

Key Concepts and Summary

The sequence of individual steps, or elementary reactions, by which reactants are converted into products during the course of a reaction is called the reaction mechanism. The overall rate of a reaction is determined by the rate of the slowest step, called the rate-determining step. Unimolecular elementary reactions have first-order rate laws, while bimolecular elementary reactions have second-order rate laws. By comparing the rate laws derived from a reaction mechanism to that determined experimentally, the mechanism may be deemed either incorrect or plausible.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Why are elementary reactions involving three or more reactants very uncommon?

Exercise:

Problem:

In general, can we predict the effect of doubling the concentration of A on the rate of the overall reaction $A + B \longrightarrow C$? Can we predict the effect if the reaction is known to be an elementary reaction?

Solution:

No. In general, for the overall reaction, we cannot predict the effect of changing the concentration without knowing the rate equation. Yes. If the reaction is an elementary reaction, then doubling the concentration of A doubles the rate.

Exercise:

Problem: Define these terms:

- (a) unimolecular reaction
- (b) bimolecular reaction
- (c) elementary reaction
- (d) overall reaction

Exercise:

Problem:

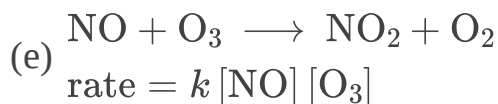
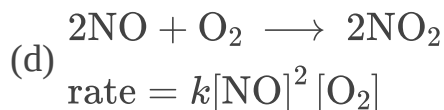
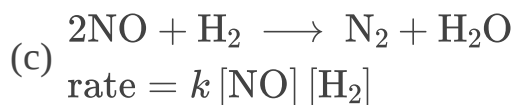
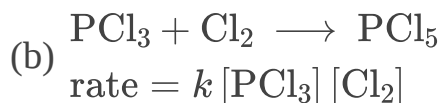
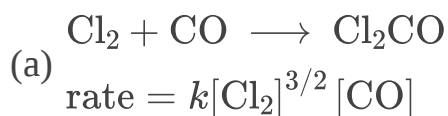
What is the rate equation for the elementary termolecular reaction $A + 2B \longrightarrow \text{products}$? For $3A \longrightarrow \text{products}$?

Solution:

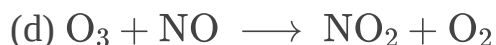
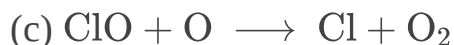
$$\text{Rate} = k[A][B]^2; \text{Rate} = k[A]^3$$

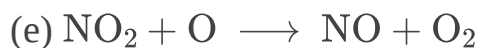
Exercise:**Problem:**

Given the following reactions and the corresponding rate laws, in which of the reactions might the elementary reaction and the overall reaction be the same?

**Exercise:****Problem:**

Write the rate equation for each of the following elementary reactions:





Solution:

(a) $\text{Rate}_1 = k[\text{O}_3]$; (b) $\text{Rate}_2 = k[\text{O}_3][\text{Cl}]$; (c) $\text{Rate}_3 = k[\text{ClO}][\text{O}]$; (d) $\text{Rate}_2 = k[\text{O}_3][\text{NO}]$; (e) $\text{Rate}_3 = k[\text{NO}_2][\text{O}]$

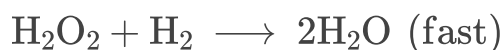
Exercise:

Problem:

Nitrogen monoxide, NO, reacts with hydrogen, H_2 , according to the following equation:



What would the rate law be if the mechanism for this reaction were:



Exercise:

Problem:

Experiments were conducted to study the rate of the reaction represented by this equation.[\[footnote\]](#)



This question is taken from the Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

Initial concentrations and rates of reaction are given here.

Experiment	Initial Concentration [NO] (mol/L)	Initial Concentration, [H ₂] (mol/L)	Initial Rate of Formation of N ₂ (mol/L min)
1	0.0060	0.0010	1.8×10^{-4}
2	0.0060	0.0020	3.6×10^{-4}
3	0.0010	0.0060	0.30×10^{-4}
4	0.0020	0.0060	1.2×10^{-4}

Consider the following questions:

(a) Determine the order for each of the reactants, NO and H₂, from the data given and show your reasoning.

(b) Write the overall rate law for the reaction.

(c) Calculate the value of the rate constant, k , for the reaction. Include units.

(d) For experiment 2, calculate the concentration of NO remaining when exactly one-half of the original amount of H₂ had been consumed.

(e) The following sequence of elementary steps is a proposed mechanism for the reaction.



Based on the data presented, which of these is the rate determining step? Show that the mechanism is consistent with the observed rate law for the reaction and the overall stoichiometry of the reaction.

Solution:

(a) Doubling $[\text{H}_2]$ doubles the rate. $[\text{H}_2]$ must enter the rate equation to the first power. Doubling $[\text{NO}]$ increases the rate by a factor of 4. $[\text{NO}]$ must enter the rate law to the second power. (b) $\text{Rate} = k [\text{NO}]^2[\text{H}_2]$; (c) $k = 5.0 \times 10^3 \text{ mol}^{-2} \text{ L}^{-2} \text{ min}^{-1}$; (d) 0.0050 mol/L ; (e) Step II is the rate-determining step. If step I gives N_2O_2 in adequate amount, steps 1 and 2 combine to give $2\text{NO} + \text{H}_2 \longrightarrow \text{H}_2\text{O} + \text{N}_2\text{O}$. This reaction corresponds to the observed rate law. Combine steps 1 and 2 with step 3, which occurs by supposition in a rapid fashion, to give the appropriate stoichiometry.

Exercise:

Problem:

The reaction of CO with Cl_2 gives phosgene (COCl_2), a nerve gas that was used in World War I. Use the mechanism shown here to complete the following exercises:

$\text{Cl}_2(g) \rightleftharpoons 2\text{Cl}(g)$ (fast, k_1 represents the forward rate constant, k_{-1} the reverse rate constant)

$\text{CO}(g) + \text{Cl}(g) \longrightarrow \text{COCl}(g)$ (slow, k_2 the rate constant)

$\text{COCl}(g) + \text{Cl}(g) \longrightarrow \text{COCl}_2(g)$ (fast, k_3 the rate constant)

- (a) Write the overall reaction.
- (b) Identify all intermediates.
- (c) Write the rate law for each elementary reaction.
- (d) Write the overall rate law expression.

Glossary

bimolecular reaction

elementary reaction involving the collision and combination of two reactant species

elementary reaction

reaction that takes place precisely as depicted in its chemical equation

intermediate

molecule or ion produced in one step of a reaction mechanism and consumed in another

molecularity

number of reactant species (atoms, molecules or ions) involved in an elementary reaction

rate-determining step

(also, rate-limiting step) slowest elementary reaction in a reaction mechanism; determines the rate of the overall reaction

reaction mechanism

stepwise sequence of elementary reactions by which a chemical change takes place

termolecular reaction

elementary reaction involving the simultaneous collision and combination of three reactant species

unimolecular reaction

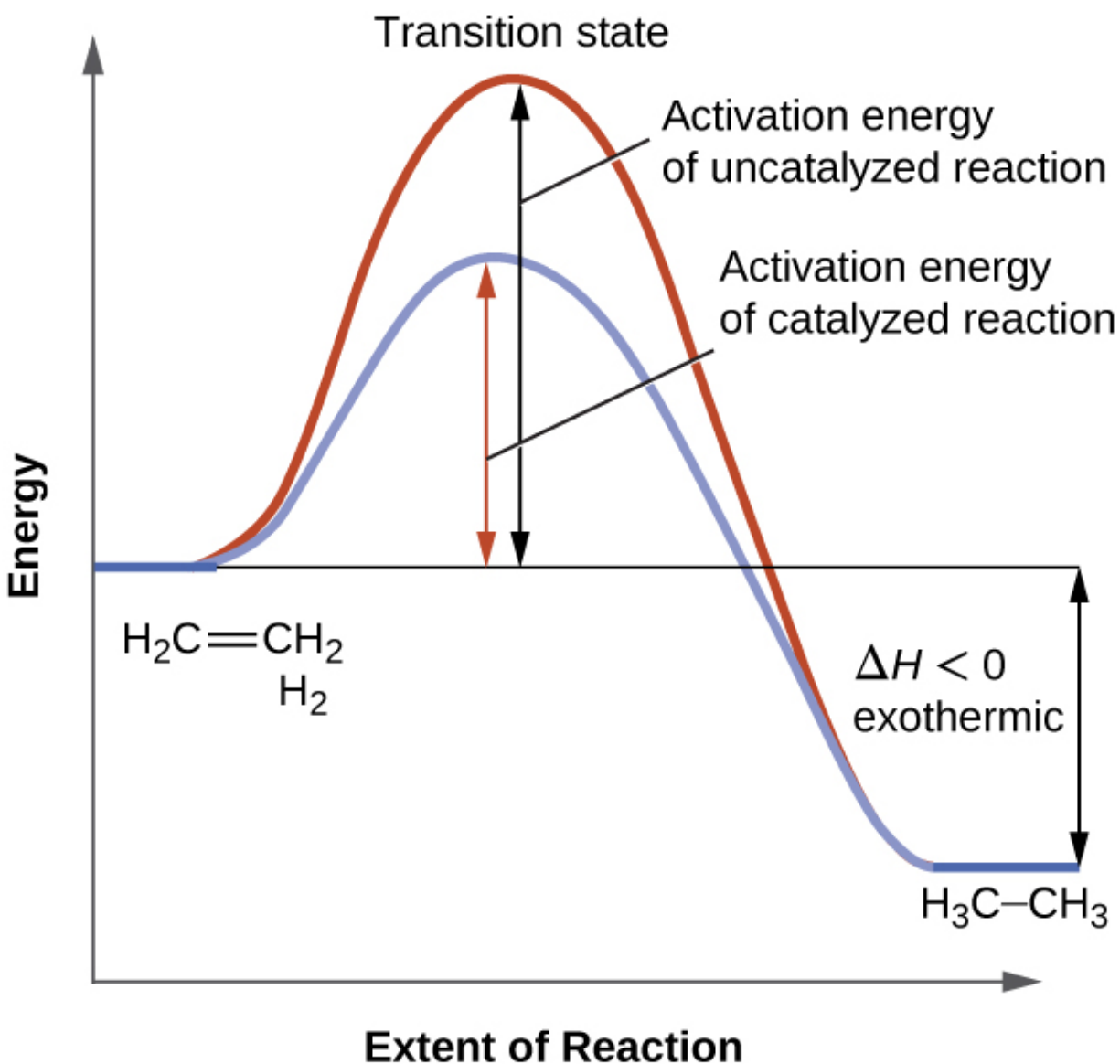
elementary reaction involving the rearrangement of a single reactant species to produce one or more molecules of product

Catalysis

By the end of this section, you will be able to:

- Explain the function of a catalyst in terms of reaction mechanisms and potential energy diagrams
- List examples of catalysis in natural and industrial processes

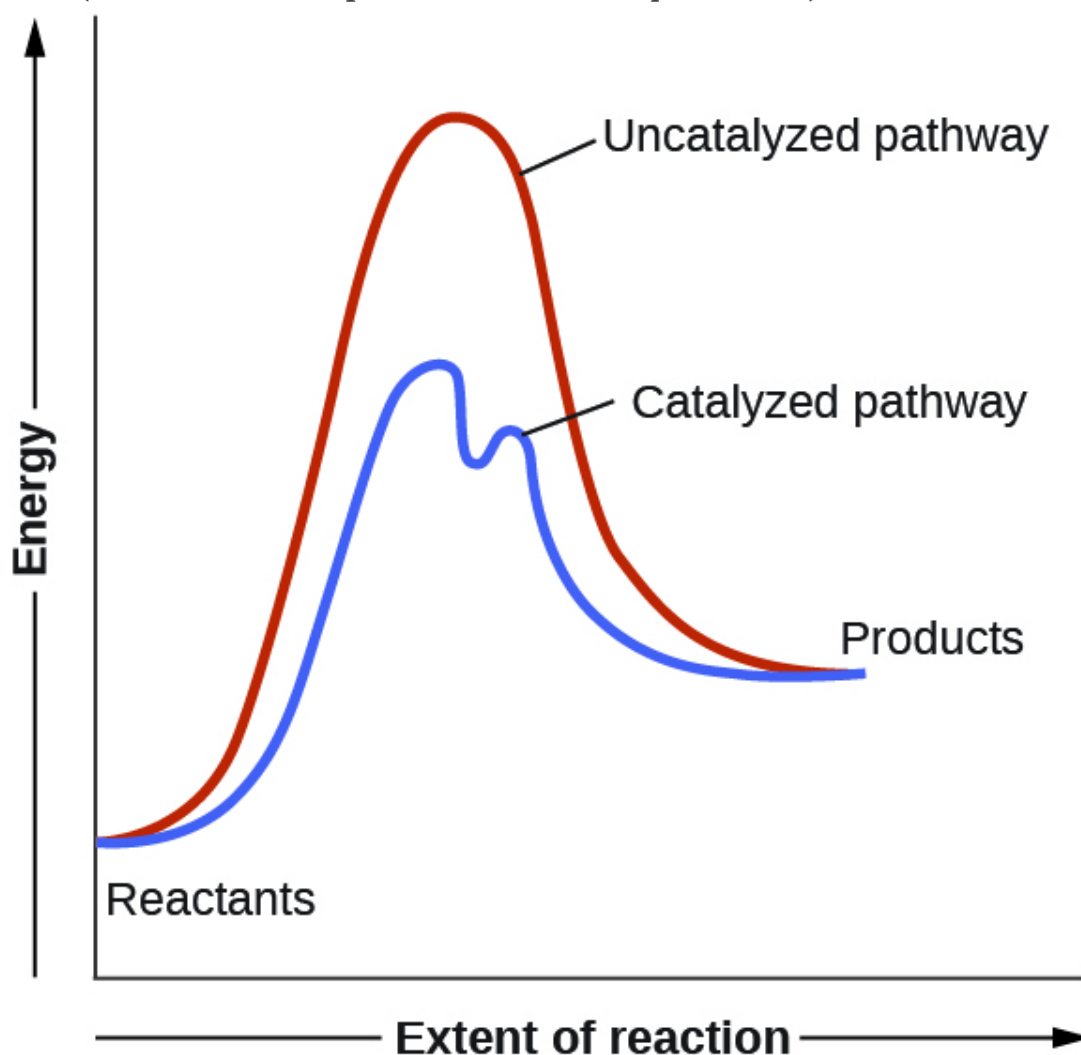
We have seen that the rate of many reactions can be accelerated by catalysts. A catalyst speeds up the rate of a reaction by lowering the activation energy; in addition, the catalyst is regenerated in the process. Several reactions that are energetically favorable in the absence of a catalyst only occur at a reasonable rate when a catalyst is present. One example is hydrogenation, a process used in food industries to convert unsaturated fats to saturated fats. A comparison of the reaction coordinate diagrams (also known as energy diagrams) for catalyzed and uncatalyzed hydrogenation of a simple hydrocarbon molecule is shown in [\[link\]](#).



This graph compares the reaction coordinates for catalyzed and uncatalyzed alkene hydrogenation.

Catalysts function by providing an alternate reaction mechanism that has a lower activation energy than would be found in the absence of the catalyst. In some cases, the catalyzed mechanism may include additional steps, as depicted in the reaction diagrams shown in [\[link\]](#). This lower activation energy results in an increase in rate as described by the Arrhenius equation. Note that a catalyst decreases the activation energy for both the forward and

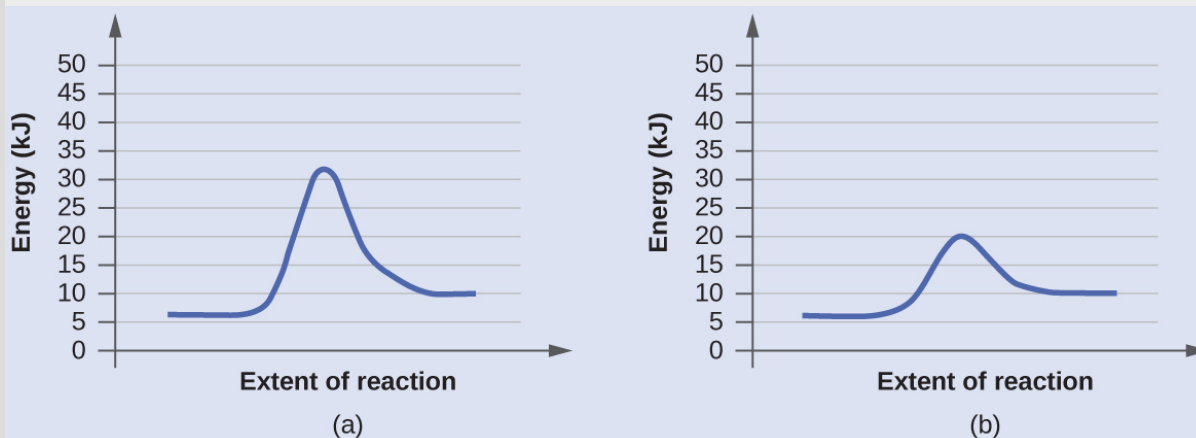
the reverse reactions and hence *accelerates both the forward and the reverse reactions*. Consequently, the presence of a catalyst will permit a system to reach equilibrium more quickly, but it has no effect on the position of the equilibrium as reflected in the value of its equilibrium constant (see the later chapter on chemical equilibrium).



This potential energy diagram shows the effect of a catalyst on the activation energy. The catalyst provides a different reaction path with a lower activation energy. As shown, the catalyzed pathway involves a two-step mechanism (note the presence of two transition states) and an intermediate species (represented by the valley between the two transitions states).

Example:**Using Reaction Diagrams to Compare Catalyzed Reactions**

The two reaction diagrams here represent the same reaction: one without a catalyst and one with a catalyst. Identify which diagram suggests the presence of a catalyst, and determine the activation energy for the catalyzed reaction:

**Solution**

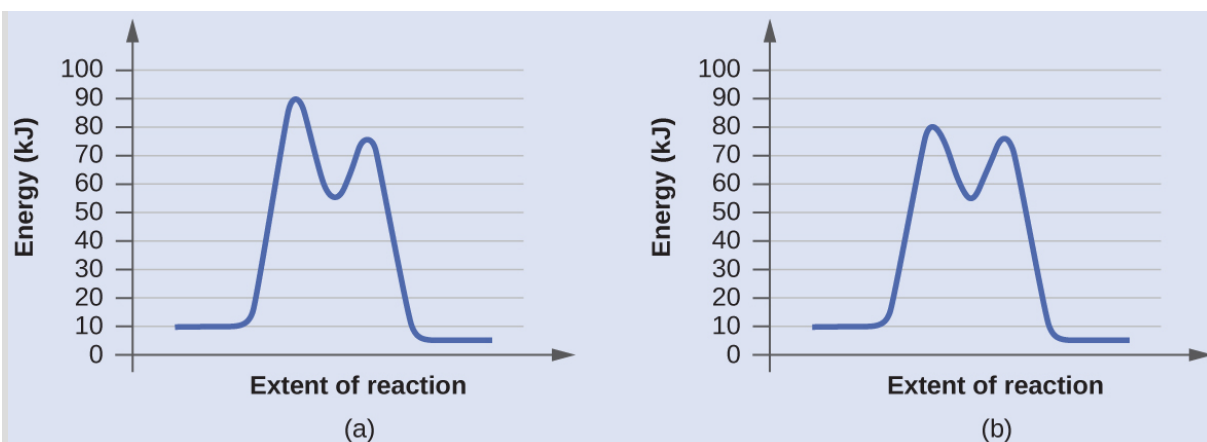
A catalyst does not affect the energy of reactant or product, so those aspects of the diagrams can be ignored; they are, as we would expect, identical in that respect. There is, however, a noticeable difference in the transition state, which is distinctly lower in diagram (b) than it is in (a). This indicates the use of a catalyst in diagram (b). The activation energy is the difference between the energy of the starting reagents and the transition state—a maximum on the reaction coordinate diagram. The reagents are at 6 kJ and the transition state is at 20 kJ, so the activation energy can be calculated as follows:

Equation:

$$E_a = 20 \text{ kJ} - 6 \text{ kJ} = 14 \text{ kJ}$$

Check Your Learning

Determine which of the two diagrams here (both for the same reaction) involves a catalyst, and identify the activation energy for the catalyzed reaction:



Note:

Answer:

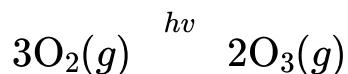
Diagram (b) is a catalyzed reaction with an activation energy of about 70 kJ.

Homogeneous Catalysts

A **homogeneous catalyst** is present in the same phase as the reactants. It interacts with a reactant to form an intermediate substance, which then decomposes or reacts with another reactant in one or more steps to regenerate the original catalyst and form product.

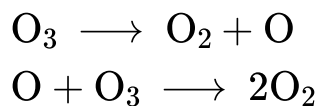
As an important illustration of homogeneous catalysis, consider the earth's ozone layer. Ozone in the upper atmosphere, which protects the earth from ultraviolet radiation, is formed when oxygen molecules absorb ultraviolet light and undergo the reaction:

Equation:



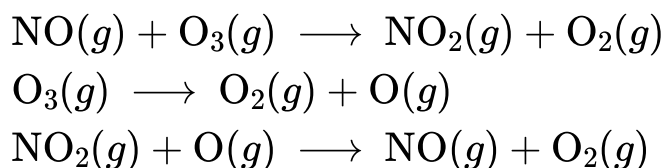
Ozone is a relatively unstable molecule that decomposes to yield diatomic oxygen by the reverse of this equation. This decomposition reaction is consistent with the following mechanism:

Equation:



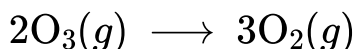
The presence of nitric oxide, NO, influences the rate of decomposition of ozone. Nitric oxide acts as a catalyst in the following mechanism:

Equation:



The overall chemical change for the catalyzed mechanism is the same as:

Equation:



The nitric oxide reacts and is regenerated in these reactions. It is not permanently used up; thus, it acts as a catalyst. The rate of decomposition of ozone is greater in the presence of nitric oxide because of the catalytic activity of NO. Certain compounds that contain chlorine also catalyze the decomposition of ozone.

Note:

Mario J. Molina

The 1995 Nobel Prize in Chemistry was shared by Paul J. Crutzen, Mario J. Molina ([\[link\]](#)), and F. Sherwood Rowland “for their work in atmospheric chemistry, particularly concerning the formation and

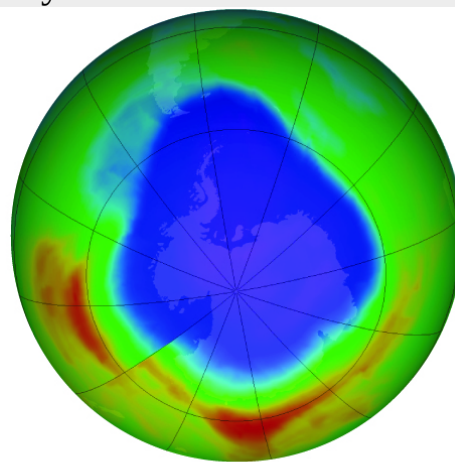
decomposition of ozone.”[\[footnote\]](#) Molina, a Mexican citizen, carried out the majority of his work at the Massachusetts Institute of Technology (MIT).

“The Nobel Prize in Chemistry 1995,” Nobel Prize.org, accessed February 18, 2015,

http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1995/.



(a)



(b)

(a) Mexican chemist Mario Molina (1943 –) shared the Nobel Prize in Chemistry in 1995 for his research on (b) the Antarctic ozone hole. (credit a: courtesy of Mario Molina; credit b: modification of work by NASA)

In 1974, Molina and Rowland published a paper in the journal *Nature* (one of the major peer-reviewed publications in the field of science) detailing the threat of chlorofluorocarbon gases to the stability of the ozone layer in earth’s upper atmosphere. The ozone layer protects earth from solar radiation by absorbing ultraviolet light. As chemical reactions deplete the amount of ozone in the upper atmosphere, a measurable “hole” forms above Antarctica, and an increase in the amount of solar ultraviolet radiation— strongly linked to the prevalence of skin cancers—reaches earth’s surface. The work of Molina and Rowland was instrumental in the adoption of the Montreal Protocol, an international treaty signed in 1987 that successfully began phasing out production of chemicals linked to ozone destruction.

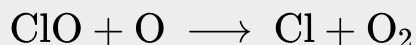
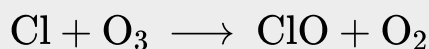
Molina and Rowland demonstrated that chlorine atoms from human-made chemicals can catalyze ozone destruction in a process similar to that by which NO accelerates the depletion of ozone. Chlorine atoms are generated when chlorocarbons or chlorofluorocarbons—once widely used as refrigerants and propellants—are photochemically decomposed by ultraviolet light or react with hydroxyl radicals. A sample mechanism is shown here using methyl chloride:

Equation:



Chlorine radicals break down ozone and are regenerated by the following catalytic cycle:

Equation:



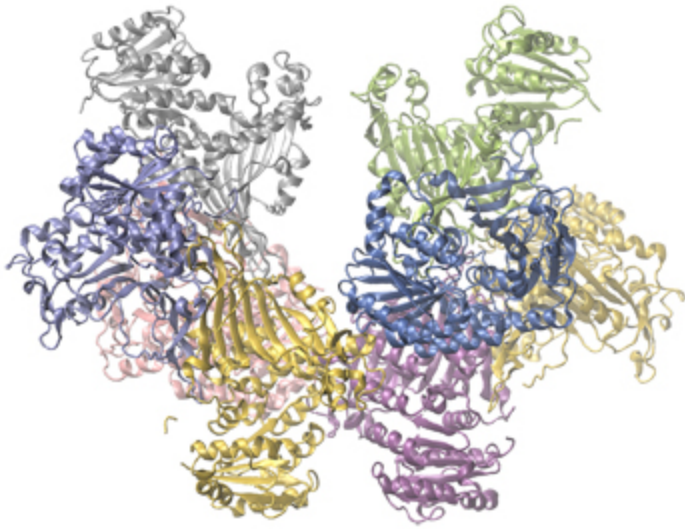
A single monatomic chlorine can break down thousands of ozone molecules. Luckily, the majority of atmospheric chlorine exists as the catalytically inactive forms Cl_2 and ClONO_2 .

Since receiving his portion of the Nobel Prize, Molina has continued his work in atmospheric chemistry at MIT.

Note:

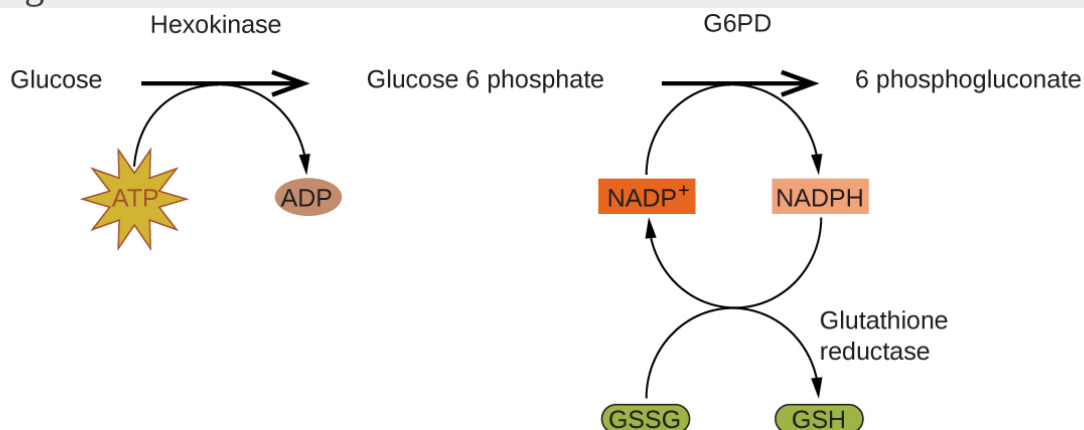
Glucose-6-Phosphate Dehydrogenase Deficiency

Enzymes in the human body act as catalysts for important chemical reactions in cellular metabolism. As such, a deficiency of a particular enzyme can translate to a life-threatening disease. G6PD (glucose-6-phosphate dehydrogenase) deficiency, a genetic condition that results in a shortage of the enzyme glucose-6-phosphate dehydrogenase, is the most common enzyme deficiency in humans. This enzyme, shown in [\[link\]](#), is the rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells ([\[link\]](#)).



Glucose-6-phosphate dehydrogenase is a rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells.

A disruption in this pathway can lead to reduced glutathione in red blood cells; once all glutathione is consumed, enzymes and other proteins such as hemoglobin are susceptible to damage. For example, hemoglobin can be metabolized to bilirubin, which leads to jaundice, a condition that can become severe. People who suffer from G6PD deficiency must avoid certain foods and medicines containing chemicals that can trigger damage their glutathione-deficient red blood cells.



In the mechanism for the pentose phosphate pathway, G6PD catalyzes

the reaction that regulates NADPH, a co-enzyme that regulates glutathione, an antioxidant that protects red blood cells and other cells from oxidative damage.

Heterogeneous Catalysts

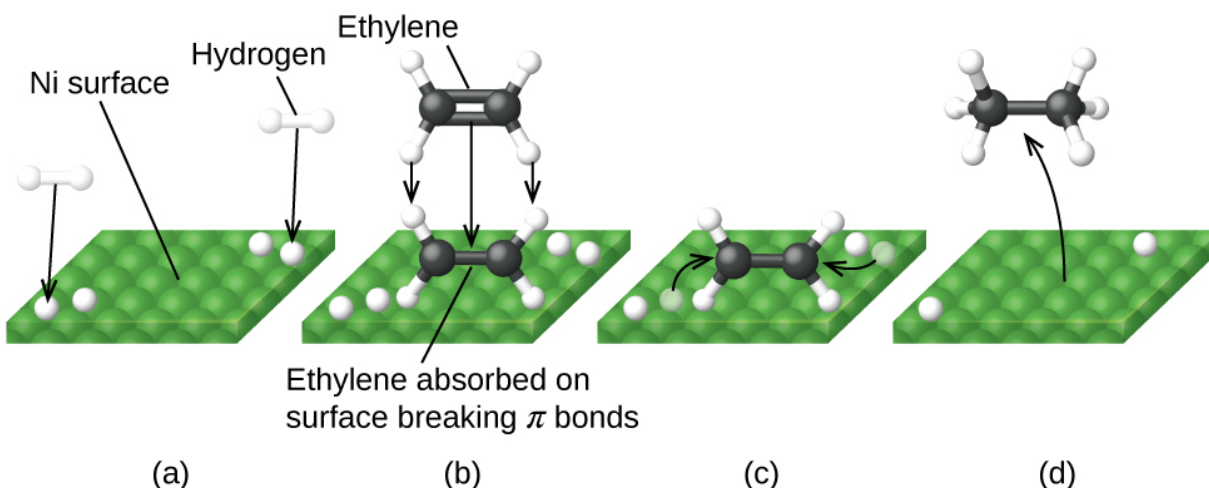
A **heterogeneous catalyst** is a catalyst that is present in a different phase (usually a solid) than the reactants. Such catalysts generally function by furnishing an active surface upon which a reaction can occur. Gas and liquid phase reactions catalyzed by heterogeneous catalysts occur on the surface of the catalyst rather than within the gas or liquid phase.

Heterogeneous catalysis has at least four steps:

1. Adsorption of the reactant onto the surface of the catalyst
2. Activation of the adsorbed reactant
3. Reaction of the adsorbed reactant
4. Diffusion of the product from the surface into the gas or liquid phase (desorption).

Any one of these steps may be slow and thus may serve as the rate determining step. In general, however, in the presence of the catalyst, the overall rate of the reaction is faster than it would be if the reactants were in the gas or liquid phase.

[\[link\]](#) illustrates the steps that chemists believe to occur in the reaction of compounds containing a carbon–carbon double bond with hydrogen on a nickel catalyst. Nickel is the catalyst used in the hydrogenation of polyunsaturated fats and oils (which contain several carbon–carbon double bonds) to produce saturated fats and oils (which contain only carbon–carbon single bonds).



There are four steps in the catalysis of the reaction $\text{C}_2\text{H}_4 + \text{H}_2 \longrightarrow \text{C}_2\text{H}_6$ by nickel. (a) Hydrogen is adsorbed on the surface, breaking the H-H bonds and forming Ni-H bonds. (b) Ethylene is adsorbed on the surface, breaking the π -bond and forming Ni-C bonds. (c) Atoms diffuse across the surface and form new C-H bonds when they collide. (d) C_2H_6 molecules escape from the nickel surface, since they are not strongly attracted to nickel.

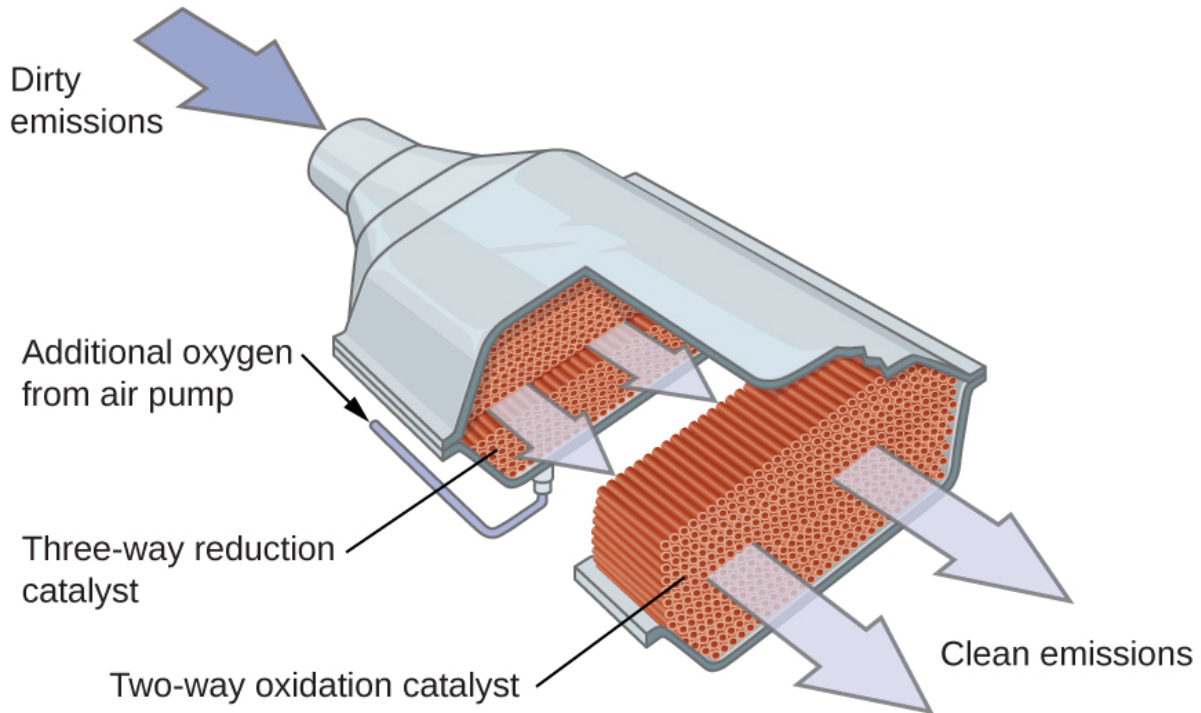
Other significant industrial processes that involve the use of heterogeneous catalysts include the preparation of sulfuric acid, the preparation of ammonia, the oxidation of ammonia to nitric acid, and the synthesis of methanol, CH_3OH . Heterogeneous catalysts are also used in the catalytic converters found on most gasoline-powered automobiles ([\[link\]](#)).

Note:

Automobile Catalytic Converters

Scientists developed catalytic converters to reduce the amount of toxic emissions produced by burning gasoline in internal combustion engines. Catalytic converters take advantage of all five factors that affect the speed of chemical reactions to ensure that exhaust emissions are as safe as possible.

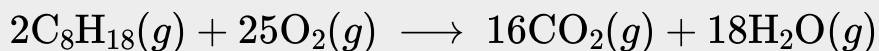
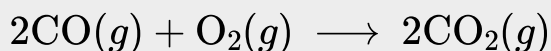
By utilizing a carefully selected blend of catalytically active metals, it is possible to effect complete combustion of all carbon-containing compounds to carbon dioxide while also reducing the output of nitrogen oxides. This is particularly impressive when we consider that one step involves adding more oxygen to the molecule and the other involves removing the oxygen ([\[link\]](#)).



A catalytic converter allows for the combustion of all carbon-containing compounds to carbon dioxide, while at the same time reducing the output of nitrogen oxide and other pollutants in emissions from gasoline-burning engines.

Most modern, three-way catalytic converters possess a surface impregnated with a platinum-rhodium catalyst, which catalyzes the conversion of nitric oxide into dinitrogen and oxygen as well as the conversion of carbon monoxide and hydrocarbons such as octane into carbon dioxide and water vapor:

Equation:



In order to be as efficient as possible, most catalytic converters are preheated by an electric heater. This ensures that the metals in the catalyst are fully active even before the automobile exhaust is hot enough to maintain appropriate reaction temperatures.

Note:



The University of California at Davis' "ChemWiki" provides a [thorough explanation](#) of how catalytic converters work.

Note:

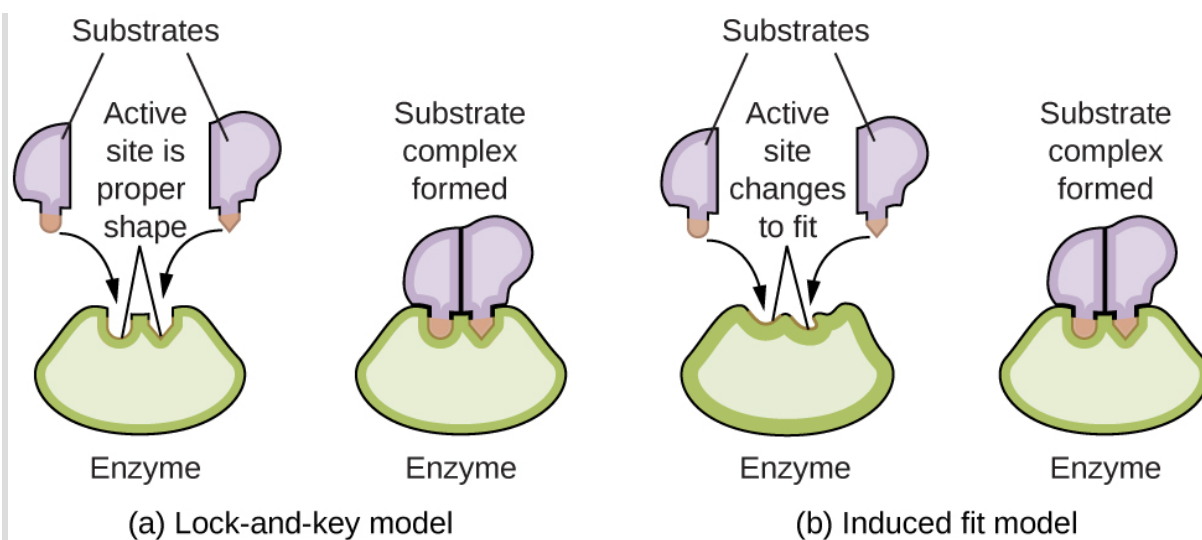
Enzyme Structure and Function

The study of enzymes is an important interconnection between biology and chemistry. Enzymes are usually proteins (polypeptides) that help to control the rate of chemical reactions between biologically important compounds, particularly those that are involved in cellular metabolism. Different classes of enzymes perform a variety of functions, as shown in [\[link\]](#).

Classes of Enzymes and Their Functions

Class	Function
oxidoreductases	redox reactions
transferases	transfer of functional groups
hydrolases	hydrolysis reactions
lyases	group elimination to form double bonds
isomerases	isomerization
ligases	bond formation with ATP hydrolysis

Enzyme molecules possess an active site, a part of the molecule with a shape that allows it to bond to a specific substrate (a reactant molecule), forming an enzyme-substrate complex as a reaction intermediate. There are two models that attempt to explain how this active site works. The most simplistic model is referred to as the lock-and-key hypothesis, which suggests that the molecular shapes of the active site and substrate are complementary, fitting together like a key in a lock. The induced fit hypothesis, on the other hand, suggests that the enzyme molecule is flexible and changes shape to accommodate a bond with the substrate. This is not to suggest that an enzyme's active site is completely malleable, however. Both the lock-and-key model and the induced fit model account for the fact that enzymes can only bind with specific substrates, since in general a particular enzyme only catalyzes a particular reaction ([\[link\]](#)).



(a) According to the lock-and-key model, the shape of an enzyme's active site is a perfect fit for the substrate. (b) According to the induced fit model, the active site is somewhat flexible, and can change shape in order to bond with the substrate.

Note:



The [Royal Society of Chemistry](https://www.rsc.org/learning/teaching-resources/chemistry-for-teachers/teaching-topics/enzymes) provides an excellent introduction to enzymes for students and teachers.

Key Concepts and Summary

Catalysts affect the rate of a chemical reaction by altering its mechanism to provide a lower activation energy. Catalysts can be homogenous (in the same phase as the reactants) or heterogeneous (a different phase than the reactants).

Chemistry End of Chapter Exercises

Exercise:

Problem:

Account for the increase in reaction rate brought about by a catalyst.

Solution:

The general mode of action for a catalyst is to provide a mechanism by which the reactants can unite more readily by taking a path with a lower reaction energy. The rates of both the forward and the reverse reactions are increased, leading to a faster achievement of equilibrium.

Exercise:

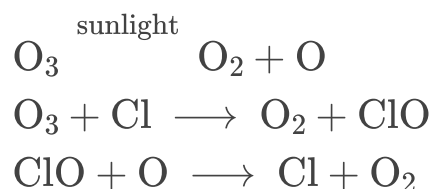
Problem:

Compare the functions of homogeneous and heterogeneous catalysts.

Exercise:

Problem:

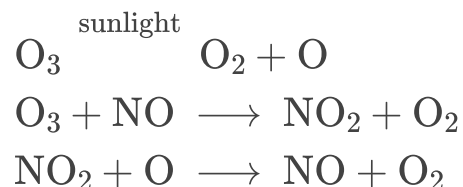
Consider this scenario and answer the following questions: Chlorine atoms resulting from decomposition of chlorofluoromethanes, such as CCl_2F_2 , catalyze the decomposition of ozone in the atmosphere. One simplified mechanism for the decomposition is:



(a) Explain why chlorine atoms are catalysts in the gas-phase transformation:



(b) Nitric oxide is also involved in the decomposition of ozone by the mechanism:



Is NO a catalyst for the decomposition? Explain your answer.

Solution:

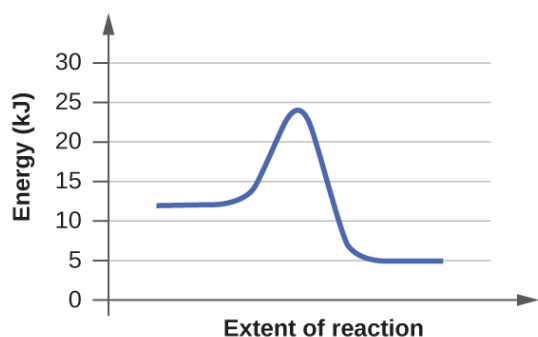
(a) Chlorine atoms are a catalyst because they react in the second step but are regenerated in the third step. Thus, they are not used up, which is a characteristic of catalysts. (b) NO is a catalyst for the same reason as in part (a).

Exercise:

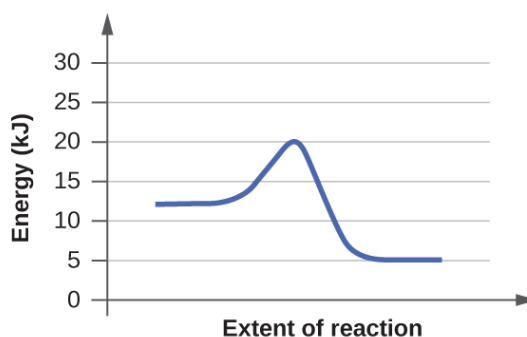
Problem:

For each of the following pairs of reaction diagrams, identify which of the pair is catalyzed:

(a)

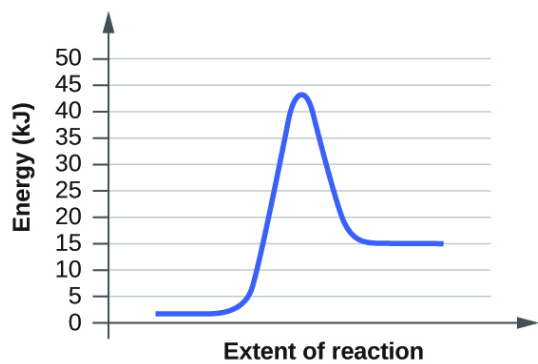


(a)



(b)

(b)



(a)



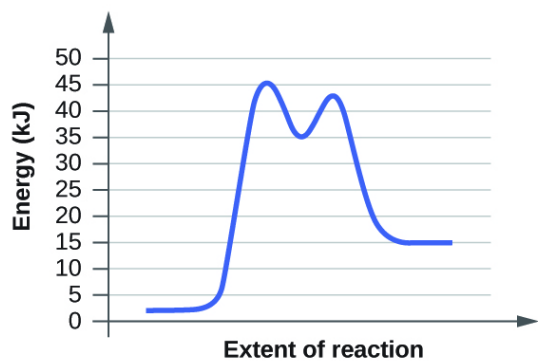
(b)

Exercise:

Problem:

For each of the following pairs of reaction diagrams, identify which of the pairs is catalyzed:

(a)

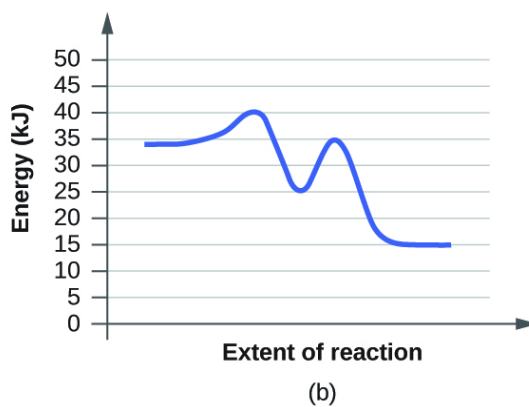
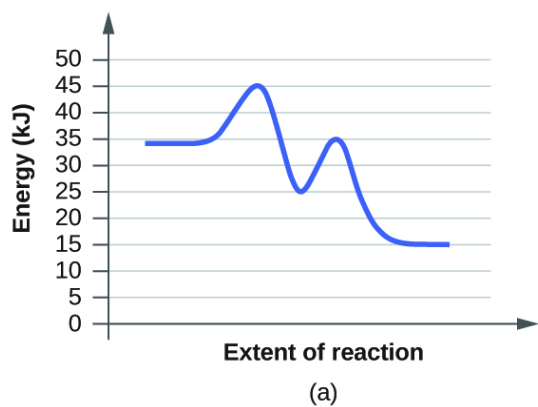


(a)



(b)

(b)



Solution:

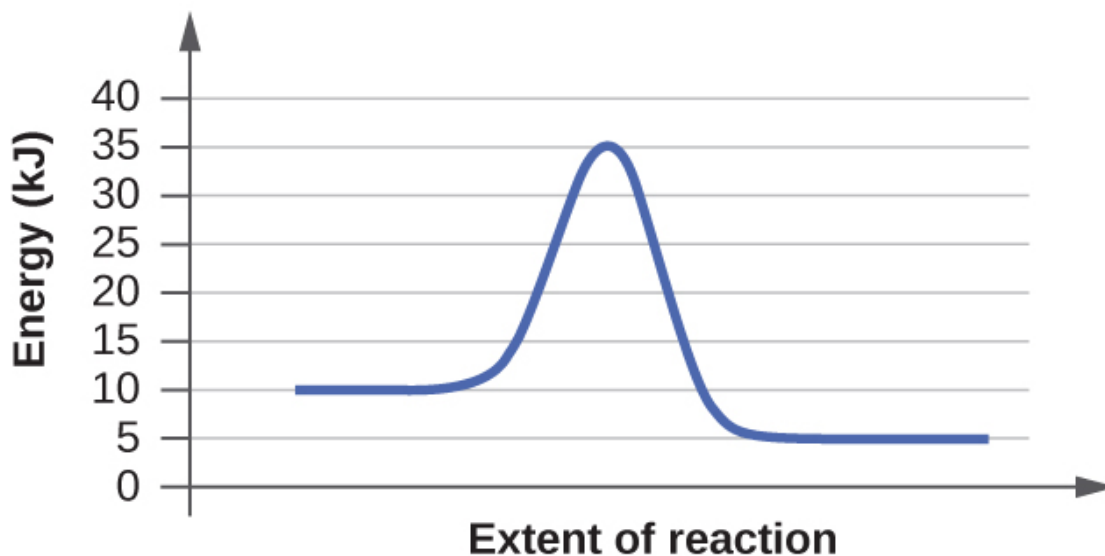
The lowering of the transition state energy indicates the effect of a catalyst. (a) B; (b) B

Exercise:

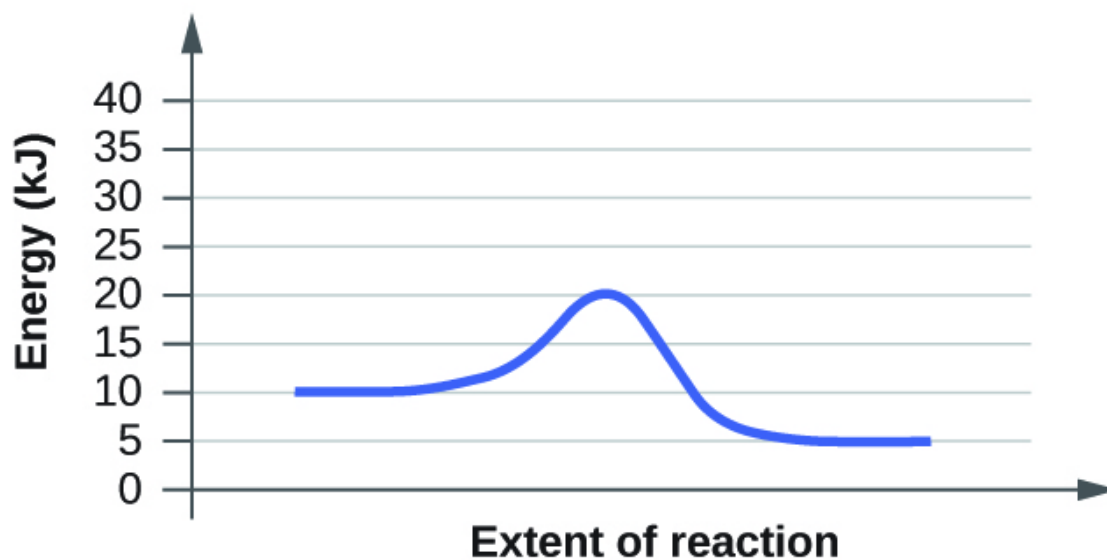
Problem:

For each of the following reaction diagrams, estimate the activation energy (E_a) of the reaction:

(a)



(b)

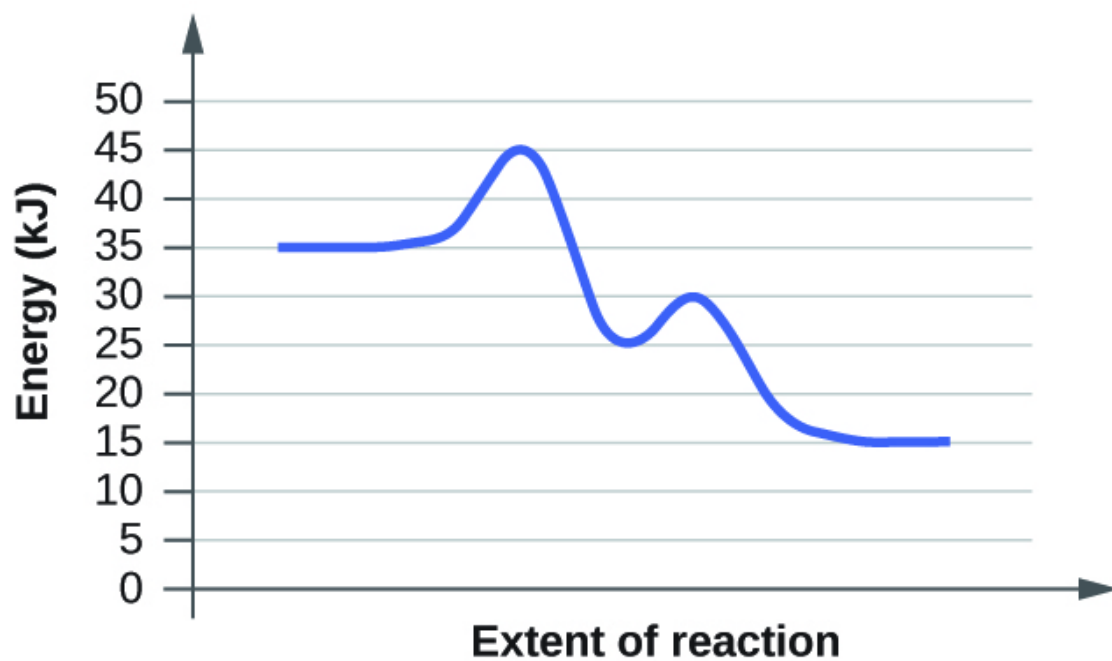


Exercise:

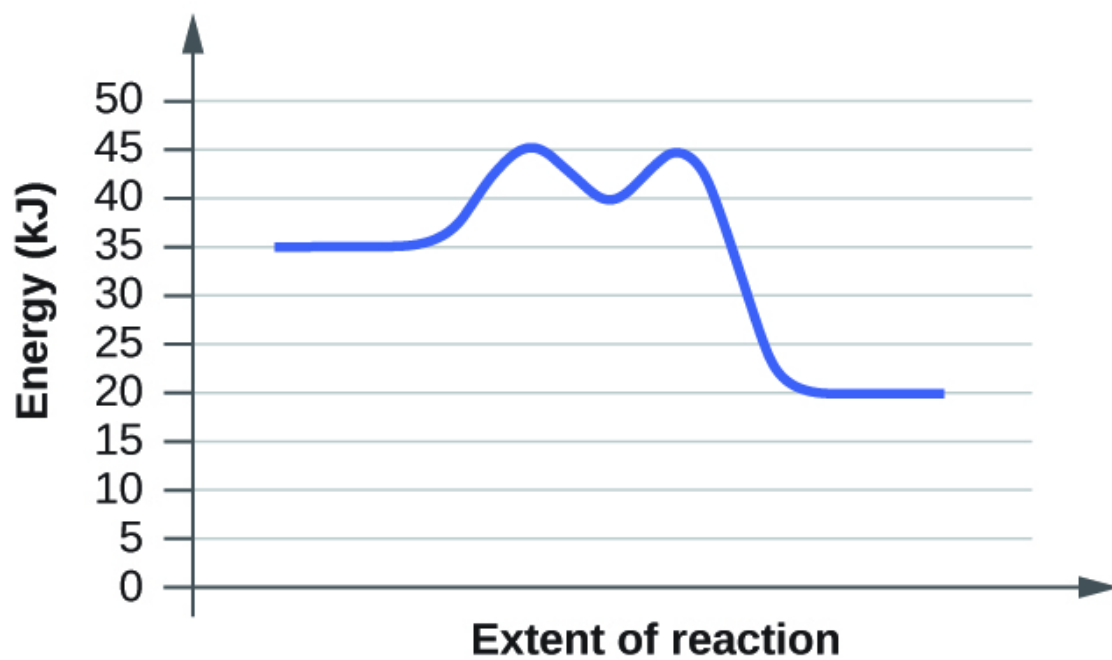
Problem:

For each of the following reaction diagrams, estimate the activation energy (E_a) of the reaction:

(a)



(b)



Solution:

The energy needed to go from the initial state to the transition state is
(a) 10 kJ; (b) 10 kJ

Exercise:

Problem:

Based on the diagrams in [\[link\]](#), which of the reactions has the fastest rate? Which has the slowest rate?

Exercise:

Problem:

Based on the diagrams in [\[link\]](#), which of the reactions has the fastest rate? Which has the slowest rate?

Solution:

Both have the same activation energy, so they also have the same rate.

Glossary

heterogeneous catalyst

catalyst present in a different phase from the reactants, furnishing a surface at which a reaction can occur

homogeneous catalyst

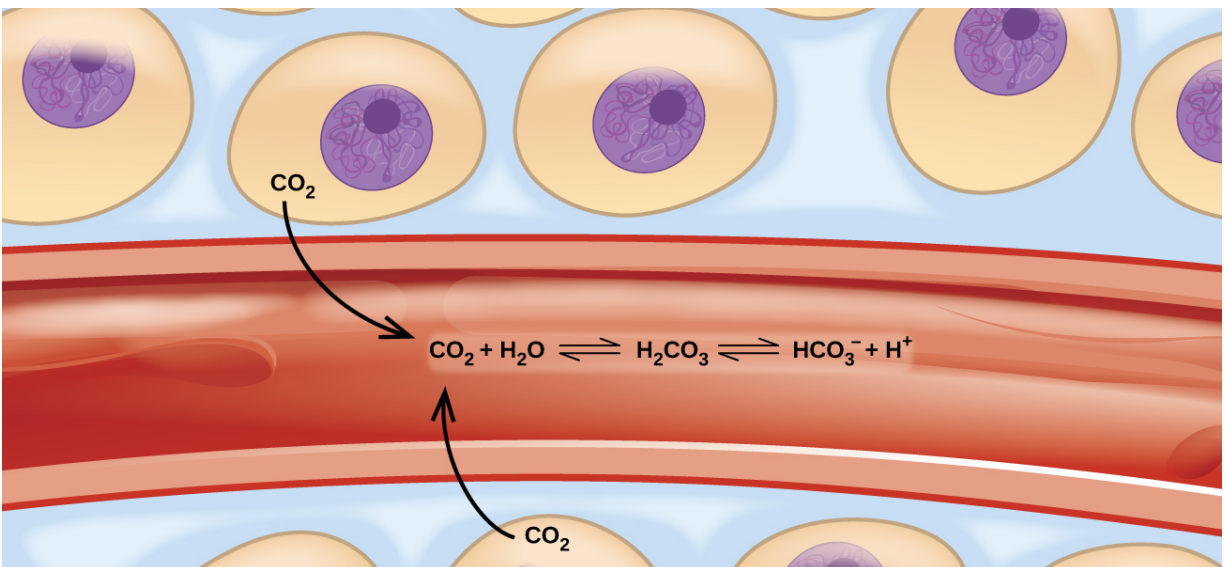
catalyst present in the same phase as the reactants

Introduction

class="introduction"

- Chemical Equilibria
- Equilibrium Constants
- Shifting Equilibria: Le Châtelier's Principle
- Equilibrium Calculations

Movement of carbon dioxide through tissues and blood cells involves several equilibrium reactions.



Imagine a beach populated with sunbathers and swimmers. As those basking in the sun get too hot and want to cool off, they head into the surf to

swim. As the swimmers tire, they head to the beach to rest. If these two rates of transfer (sunbathers entering the water, swimmers leaving the water) are equal, the number of sunbathers and swimmers would be constant, or at equilibrium, although the identities of the people are constantly changing from sunbather to swimmer and back. An analogous situation occurs in chemical reactions. Reactions can occur in both directions simultaneously (reactants to products and products to reactants) and eventually reach a state of balance.

These balanced two-way reactions occur all around and even in us. For example, they occur in our blood, where the reaction between carbon dioxide and water forms carbonic acid (H_2CO_3) ([\[link\]](#)). Human physiology is adapted to the amount of ionized products produced by this reaction (HCO_3^- and H^+). This chapter provides a thorough introduction to the essential aspects of chemical equilibria.

Chemical Equilibria

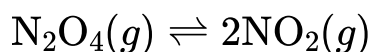
By the end of this section, you will be able to:

- Describe the nature of equilibrium systems
- Explain the dynamic nature of a chemical equilibrium

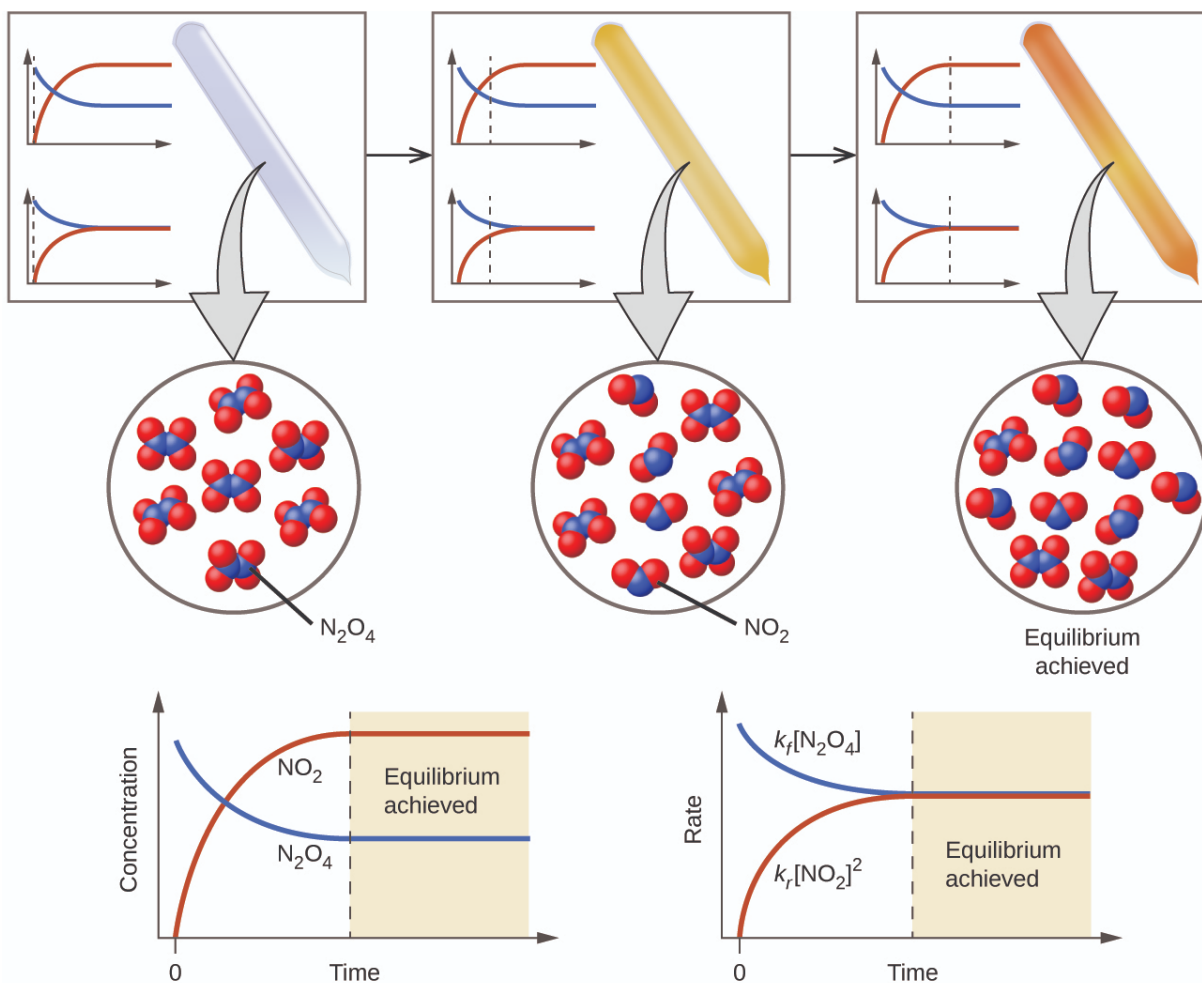
A chemical reaction is usually written in a way that suggests it proceeds in one direction, the direction in which we read, but all chemical reactions are reversible, and both the forward and reverse reaction occur to one degree or another depending on conditions. In a chemical **equilibrium**, the forward and reverse reactions occur at equal rates, and the concentrations of products and reactants remain constant. If we run a reaction in a closed system so that the products cannot escape, we often find the reaction does not give a 100% yield of products. Instead, some reactants remain after the concentrations stop changing. At this point, when there is no further change in concentrations of reactants and products, we say the reaction is at equilibrium. A mixture of reactants and products is found at equilibrium.

For example, when we place a sample of dinitrogen tetroxide (N_2O_4 , a colorless gas) in a glass tube, it forms nitrogen dioxide (NO_2 , a brown gas) by the reaction

Equation:



The color becomes darker as N_2O_4 is converted to NO_2 . When the system reaches equilibrium, both N_2O_4 and NO_2 are present ([link](#)).



A mixture of NO_2 and N_2O_4 moves toward equilibrium. Colorless N_2O_4 reacts to form brown NO_2 . As the reaction proceeds toward equilibrium, the color of the mixture darkens due to the increasing concentration of NO_2 .

The formation of NO_2 from N_2O_4 is a **reversible reaction**, which is identified by the equilibrium arrow (\rightleftharpoons). All reactions are reversible, but many reactions, for all practical purposes, proceed in one direction until the reactants are exhausted and will reverse only under certain conditions. Such reactions are often depicted with a one-way arrow from reactants to products. Many other reactions, such as the formation of NO_2 from N_2O_4 , are reversible under more easily obtainable conditions and, therefore, are

named as such. In a reversible reaction, the reactants can combine to form products and the products can react to form the reactants. Thus, not only can N_2O_4 decompose to form NO_2 , but the NO_2 produced can react to form N_2O_4 . As soon as the forward reaction produces any NO_2 , the reverse reaction begins and NO_2 starts to react to form N_2O_4 . At equilibrium, the concentrations of N_2O_4 and NO_2 no longer change because the rate of formation of NO_2 is exactly equal to the rate of consumption of NO_2 , and the rate of formation of N_2O_4 is exactly equal to the rate of consumption of N_2O_4 . *Chemical equilibrium is a dynamic process*: As with the swimmers and the sunbathers, the numbers of each remain constant, yet there is a flux back and forth between them ([link](#)).



These jugglers provide an illustration of dynamic equilibrium. Each throws clubs to the other at the same rate at which he receives clubs from that person. Because clubs are thrown continuously in both directions, the number of clubs moving in each direction is constant,

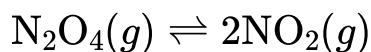
and the number of clubs each juggler has at a given time remains (roughly) constant.

In a chemical equilibrium, the forward and reverse reactions do not stop, rather they continue to occur at the same rate, leading to constant concentrations of the reactants and the products. Plots showing how the reaction rates and concentrations change with respect to time are shown in [\[link\]](#).

We can detect a state of equilibrium because the concentrations of reactants and products do not appear to change. However, it is important that we verify that the absence of change is due to equilibrium and not to a reaction rate that is so slow that changes in concentration are difficult to detect.

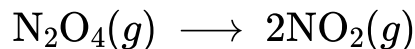
We use a double arrow when writing an equation for a reversible reaction. Such a reaction may or may not be at equilibrium. For example, [\[link\]](#) shows the reaction:

Equation:



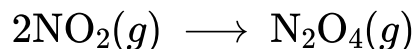
When we wish to speak about one particular component of a reversible reaction, we use a single arrow. For example, in the equilibrium shown in [\[link\]](#), the rate of the forward reaction

Equation:



is equal to the rate of the backward reaction

Equation:

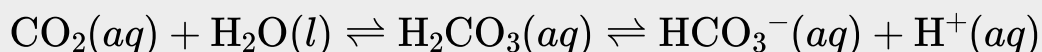


Note:**Equilibrium and Soft Drinks**

The connection between chemistry and carbonated soft drinks goes back to 1767, when Joseph Priestley (1733–1804; mostly known today for his role in the discovery and identification of oxygen) discovered a method of infusing water with carbon dioxide to make carbonated water. In 1772, Priestly published a paper entitled “Impregnating Water with Fixed Air.” The paper describes dripping oil of vitriol (today we call this sulfuric acid, but what a great way to describe sulfuric acid: “oil of vitriol” literally means “liquid nastiness”) onto chalk (calcium carbonate). The resulting CO_2 falls into the container of water beneath the vessel in which the initial reaction takes place; agitation helps the gaseous CO_2 mix into the liquid water.

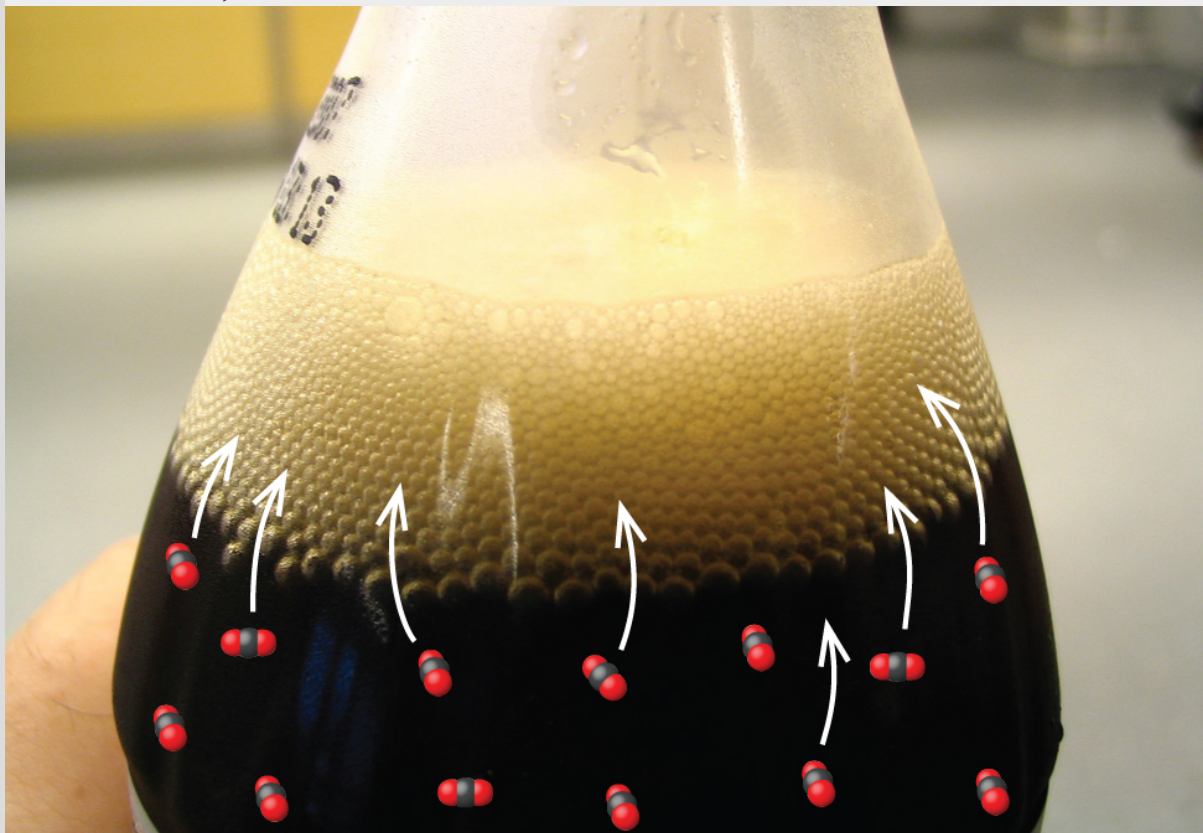
Equation:

Carbon dioxide is slightly soluble in water. There is an equilibrium reaction that occurs as the carbon dioxide reacts with the water to form carbonic acid (H_2CO_3). Since carbonic acid is a weak acid, it can dissociate into protons (H^+) and hydrogen carbonate ions (HCO_3^-).

Equation:

Today, CO_2 can be pressurized into soft drinks, establishing the equilibrium shown above. Once you open the beverage container, however, a cascade of equilibrium shifts occurs. First, the CO_2 gas in the air space on top of the bottle escapes, causing the equilibrium between gas-phase CO_2 and dissolved or aqueous CO_2 to shift, lowering the concentration of CO_2 in the soft drink. Less CO_2 dissolved in the liquid leads to carbonic acid decomposing to dissolved CO_2 and H_2O . The lowered carbonic acid concentration causes a shift of the final equilibrium. As long as the soft drink is in an open container, the CO_2 bubbles up out of the beverage, releasing the gas into the air ([\[link\]](#)). With the lid off the bottle, the CO_2 reactions are no longer at equilibrium and will continue until no more of

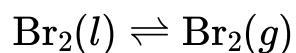
the reactants remain. This results in a soft drink with a much lowered CO₂ concentration, often referred to as “flat.”



When a soft drink is opened, several equilibrium shifts occur. (credit: modification of work by “D Coetzee”/Flickr)

Let us consider the evaporation of bromine as a second example of a system at equilibrium.

Equation:



An equilibrium can be established for a physical change—like this liquid to gas transition—as well as for a chemical reaction. [\[link\]](#) shows a sample of

liquid bromine at equilibrium with bromine vapor in a closed container. When we pour liquid bromine into an empty bottle in which there is no bromine vapor, some liquid evaporates, the amount of liquid decreases, and the amount of vapor increases. If we cap the bottle so no vapor escapes, the amount of liquid and vapor will eventually stop changing and an equilibrium between the liquid and the vapor will be established. If the bottle were not capped, the bromine vapor would escape and no equilibrium would be reached.



An equilibrium is pictured between liquid bromine, $\text{Br}_2(l)$, the dark liquid, and bromine vapor, $\text{Br}_2(g)$, the reddish-brown gas. Because the container is sealed, bromine vapor cannot escape and equilibrium is maintained. (credit: <http://images-of-elements.com/bromine.php>)

Key Concepts and Summary

A reaction is at equilibrium when the amounts of reactants or products no longer change. Chemical equilibrium is a dynamic process, meaning the rate of formation of products by the forward reaction is equal to the rate at which the products re-form reactants by the reverse reaction.

Chemistry End of Chapter Exercises

Exercise:

Problem: What does it mean to describe a reaction as “reversible”?

Solution:

The reaction can proceed in both the forward and reverse directions.

Exercise:

Problem:

When writing an equation, how is a reversible reaction distinguished from a nonreversible reaction?

Exercise:

Problem:

If a reaction is reversible, when can it be said to have reached equilibrium?

Solution:

When a system has reached equilibrium, no further changes in the reactant and product concentrations occur; the reactions continue to occur, but at equivalent rates.

Exercise:**Problem:**

Is a system at equilibrium if the rate constants of the forward and reverse reactions are equal?

Exercise:**Problem:**

If the concentrations of products and reactants are equal, is the system at equilibrium?

Solution:

The concept of equilibrium does not imply equal concentrations, though it is possible.

Glossary**equilibrium**

in chemical reactions, the state in which the conversion of reactants into products and the conversion of products back into reactants occur simultaneously at the same rate; state of balance

reversible reaction

chemical reaction that can proceed in both the forward and reverse directions under given conditions

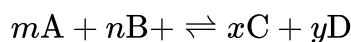
Equilibrium Constants

By the end of this section, you will be able to:

- Derive reaction quotients from chemical equations representing homogeneous and heterogeneous reactions
- Calculate values of reaction quotients and equilibrium constants, using concentrations and pressures
- Relate the magnitude of an equilibrium constant to properties of the chemical system

Now that we have a symbol (\rightleftharpoons) to designate reversible reactions, we will need a way to express mathematically how the amounts of reactants and products affect the equilibrium of the system. A general equation for a reversible reaction may be written as follows:

Equation:



We can write the **reaction quotient (Q)** for this equation. When evaluated using concentrations, it is called Q_c . We use brackets to indicate molar concentrations of reactants and products.

Equation:

$$Q_c = \frac{[C]^x [D]^y}{[A]^m [B]^n}$$

The reaction quotient is equal to the molar concentrations of the products of the chemical equation (multiplied together) over the reactants (also multiplied together), with each concentration raised to the power of the coefficient of that substance in the balanced chemical equation. For example, the reaction quotient for the reversible reaction $2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$ is given by this expression:

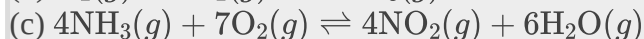
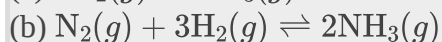
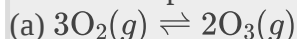
Equation:

$$Q_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$$

Example:

Writing Reaction Quotient Expressions

Write the expression for the reaction quotient for each of the following reactions:



Solution

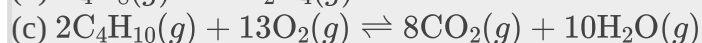
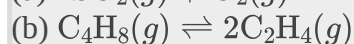
$$(a) Q_c = \frac{[\text{O}_3]^2}{[\text{O}_2]^3}$$

$$(b) Q_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

$$(c) Q_c = \frac{[\text{NO}_2]^4[\text{H}_2\text{O}]^6}{[\text{NH}_3]^4[\text{O}_2]^7}$$

Check Your Learning

Write the expression for the reaction quotient for each of the following reactions:

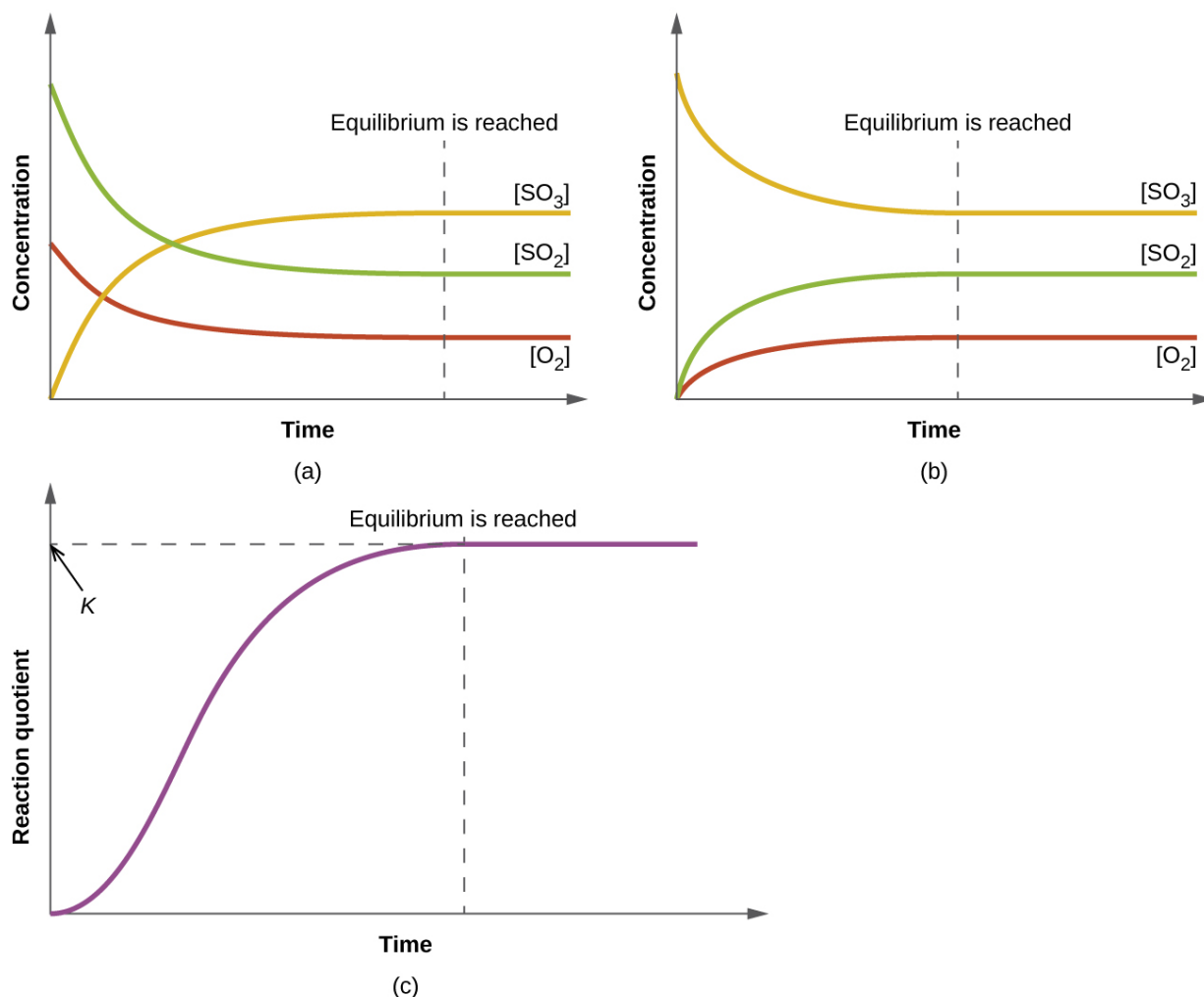


Note:

Answer:

$$(a) Q_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}; (b) Q_c = \frac{[\text{C}_2\text{H}_4]^2}{[\text{C}_4\text{H}_8]}; (c) Q_c = \frac{[\text{CO}_2]^8[\text{H}_2\text{O}]^{10}}{[\text{C}_4\text{H}_{10}]^2[\text{O}_2]^{13}}$$

The numeric value of Q_c for a given reaction varies; it depends on the concentrations of products and reactants present at the time when Q_c is determined. When pure reactants are mixed, Q_c is initially zero because there are no products present at that point. As the reaction proceeds, the value of Q_c increases as the concentrations of the products increase and the concentrations of the reactants simultaneously decrease ([link](#)). When the reaction reaches equilibrium, the value of the reaction quotient no longer changes because the concentrations no longer change.



(a) The change in the concentrations of reactants and products is depicted as the $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ reaction approaches equilibrium. (b) The change in concentrations of reactants and products is depicted as the reaction $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ approaches equilibrium. (c) The graph shows the change in the value of the reaction quotient as the reaction approaches equilibrium.

When a mixture of reactants and products of a reaction reaches equilibrium at a given temperature, its reaction quotient always has the same value. This value is called the **equilibrium constant (K)** of the reaction at that temperature. As for the reaction quotient, when evaluated in terms of concentrations, it is noted as K_c .

That a reaction quotient always assumes the same value at equilibrium can be expressed as:
Equation:

$$Q_c \text{ at equilibrium} = K_c = \frac{[C]^x[D]^y\dots}{[A]^m[B]^n\dots}$$

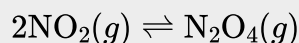
This equation is a mathematical statement of the **law of mass action**: When a reaction has attained equilibrium at a given temperature, the reaction quotient for the reaction always has the same value.

Example:

Evaluating a Reaction Quotient

Gaseous nitrogen dioxide forms dinitrogen tetroxide according to this equation:

Equation:



When 0.10 mol NO_2 is added to a 1.0-L flask at 25 °C, the concentration changes so that at equilibrium, $[\text{NO}_2] = 0.016 \text{ M}$ and $[\text{N}_2\text{O}_4] = 0.042 \text{ M}$.

(a) What is the value of the reaction quotient before any reaction occurs?

(b) What is the value of the equilibrium constant for the reaction?

Solution

(a) Before any product is formed, $[\text{NO}_2] = \frac{0.10 \text{ mol}}{1.0 \text{ L}} = 0.10 \text{ M}$, and $[\text{N}_2\text{O}_4] = 0 \text{ M}$. Thus,

Equation:

$$Q_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{0}{0.10^2} = 0$$

(b) At equilibrium, the value of the equilibrium constant is equal to the value of the reaction quotient. At equilibrium, $K_c = Q_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{0.042}{0.016^2} = 1.6 \times 10^2$. The equilibrium constant is 1.6×10^2 .

Note that dimensional analysis would suggest the unit for this K_c value should be M^{-1} .

However, it is common practice to omit units for K_c values computed as described here, since it is the magnitude of an equilibrium constant that relays useful information. As will be discussed later in this module, the rigorous approach to computing equilibrium constants uses dimensionless quantities derived from concentrations instead of actual concentrations, and so K_c values are truly unitless.

Check Your Learning

For the reaction $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$, the concentrations at equilibrium are $[\text{SO}_2] = 0.90 \text{ M}$, $[\text{O}_2] = 0.35 \text{ M}$, and $[\text{SO}_3] = 1.1 \text{ M}$. What is the value of the equilibrium constant, K_c ?

Note:

Answer:

$$K_c = 4.3$$

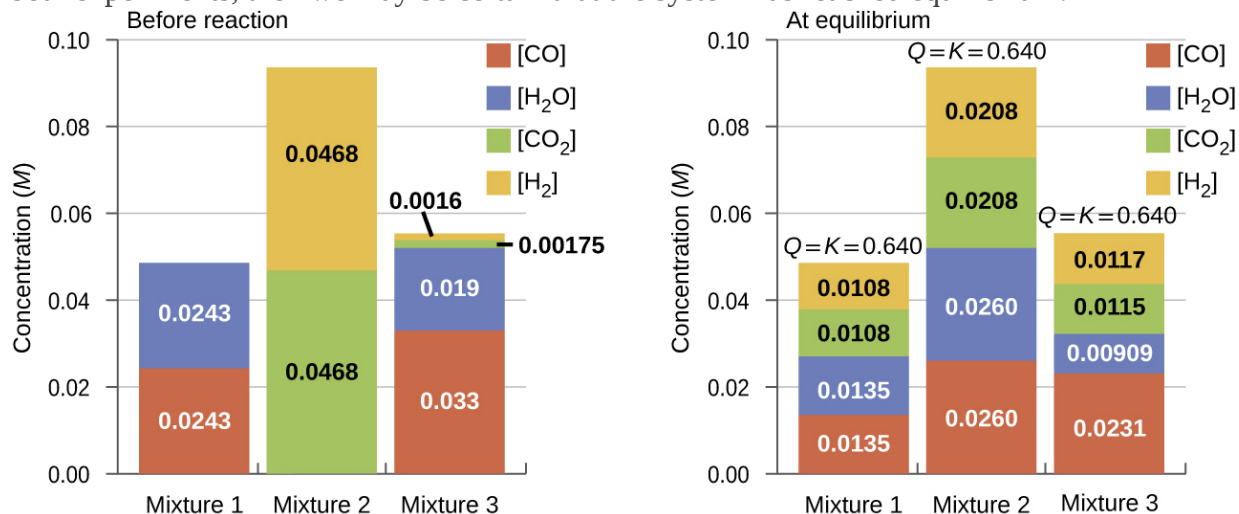
The magnitude of an equilibrium constant is a measure of the yield of a reaction when it reaches equilibrium. A large value for K_c indicates that equilibrium is attained only after the reactants have been largely converted into products. A small value of K_c —much less than 1—indicates that equilibrium is attained when only a small proportion of the reactants have been converted into products.

Once a value of K_c is known for a reaction, it can be used to predict directional shifts when compared to the value of Q_c . A system that is not at equilibrium will proceed in the direction that establishes equilibrium. The data in [\[link\]](#) illustrate this. When heated to a consistent temperature, 800 °C, different starting mixtures of CO, H₂O, CO₂, and H₂ react to reach compositions adhering to the same equilibrium constant (the value of Q_c changes until it equals the value of K_c). This value is 0.640, the equilibrium constant for the reaction under these conditions.

Equation:



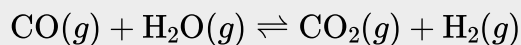
It is important to recognize that an equilibrium can be established starting either from reactants or from products, or from a mixture of both. For example, equilibrium was established from Mixture 2 in [\[link\]](#) when the products of the reaction were heated in a closed container. In fact, one technique used to determine whether a reaction is truly at equilibrium is to approach equilibrium starting with reactants in one experiment and starting with products in another. If the same value of the reaction quotient is observed when the concentrations stop changing in both experiments, then we may be certain that the system has reached equilibrium.



Concentrations of three mixtures are shown before and after reaching equilibrium at 800 °C for the so-called water gas shift reaction: $\text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)$.

Example:**Predicting the Direction of Reaction**

Given here are the starting concentrations of reactants and products for three experiments involving this reaction:

Equation:**Equation:**

$$K_c = 0.64$$

Determine in which direction the reaction proceeds as it goes to equilibrium in each of the three experiments shown.

Reactants/Products	Experiment 1	Experiment 2	Experiment 3
[CO] _i	0.0203 M	0.011 M	0.0094 M
[H ₂ O] _i	0.0203 M	0.0011 M	0.0025 M
[CO ₂] _i	0.0040 M	0.037 M	0.0015 M
[H ₂] _i	0.0040 M	0.046 M	0.0076 M

Solution

Experiment 1:

Equation:

$$Q_c = \frac{[\text{CO}_2] [\text{H}_2]}{[\text{CO}] [\text{H}_2\text{O}]} = \frac{(0.0040)(0.0040)}{(0.0203)(0.0203)} = 0.039.$$

$$Q_c < K_c \text{ (} 0.039 < 0.64 \text{)}$$

The reaction will shift to the right.

Experiment 2:

Equation:

$$Q_c = \frac{[\text{CO}_2] [\text{H}_2]}{[\text{CO}] [\text{H}_2\text{O}]} = \frac{(0.037)(0.046)}{(0.011)(0.0011)} = 1.4 \times 10^2$$

$$Q_c > K_c \text{ (} 140 > 0.64 \text{)}$$

The reaction will shift to the left.

Experiment 3:

Equation:

$$Q_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{(0.0015)(0.0076)}{(0.0094)(0.0025)} = 0.48$$

$$Q_c < K_c (0.48 < 0.64)$$

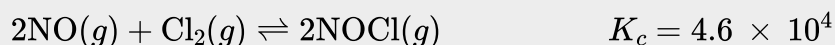
The reaction will shift to the right.

Check Your Learning

Calculate the reaction quotient and determine the direction in which each of the following reactions will proceed to reach equilibrium.

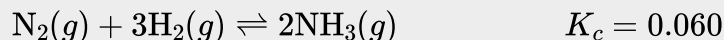
(a) A 1.00-L flask containing 0.0500 mol of NO(g), 0.0155 mol of Cl₂(g), and 0.500 mol of NOCl:

Equation:



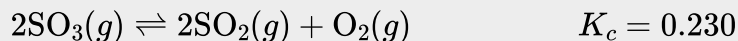
(b) A 5.0-L flask containing 17 g of NH₃, 14 g of N₂, and 12 g of H₂:

Equation:



(c) A 2.00-L flask containing 230 g of SO₃(g):

Equation:



Note:

Answer:

(a) $Q_c = 6.45 \times 10^3$, shifts right. (b) $Q_c = 0.23$, shifts left. (c) $Q_c = 0$, shifts right

In [\[link\]](#), it was mentioned that the common practice is to omit units when evaluating reaction quotients and equilibrium constants. It should be pointed out that using concentrations in these computations is a convenient but simplified approach that sometimes leads to results that seemingly conflict with the law of mass action. For example, equilibria involving aqueous ions often exhibit equilibrium constants that vary quite significantly (are *not* constant) at high solution concentrations. This may be avoided by computing K_c values using the *activities* of the reactants and products in the equilibrium system instead of their concentrations. The **activity** of a substance is a measure of its effective concentration under specified conditions.

While a detailed discussion of this important quantity is beyond the scope of an introductory text, it is necessary to be aware of a few important aspects:

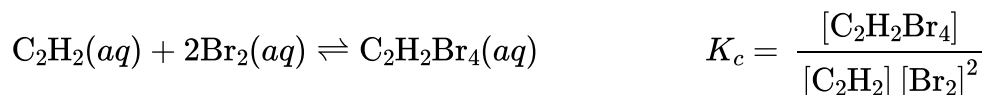
- Activities are dimensionless (unitless) quantities and are in essence “adjusted” concentrations.
- For relatively dilute solutions, a substance's activity and its molar concentration are roughly equal.
- Activities for pure condensed phases (solids and liquids) are equal to 1.

As a consequence of this last consideration, Q_c and K_c expressions do not contain terms for solids or liquids (being numerically equal to 1, these terms have no effect on the expression's value). Several examples of equilibria yielding such expressions will be encountered in this section.

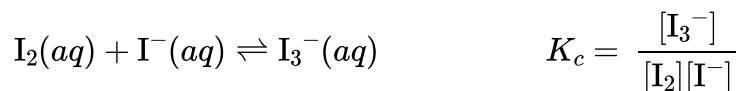
Homogeneous Equilibria

A **homogeneous equilibrium** is one in which all of the reactants and products are present in a single solution (by definition, a homogeneous mixture). In this chapter, we will concentrate on the two most common types of homogeneous equilibria: those occurring in liquid-phase solutions and those involving exclusively gaseous species. Reactions between solutes in liquid solutions belong to one type of homogeneous equilibria. The chemical species involved can be molecules, ions, or a mixture of both. Several examples are provided here.

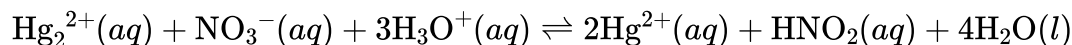
Equation:



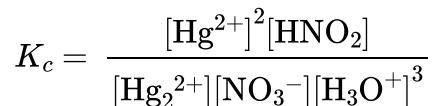
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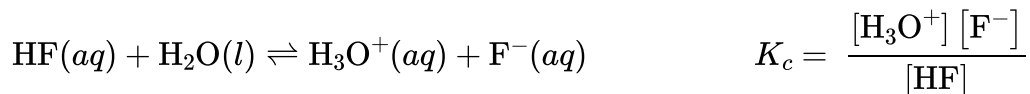
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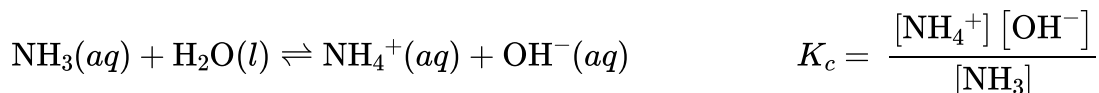
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Equation:



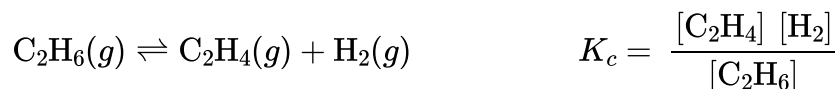
Equation:



In each of these examples, the equilibrium system is an aqueous solution, as denoted by the *aq* annotations on the solute formulas. Since $\text{H}_2\text{O}(l)$ is the solvent for these solutions, its concentration does not appear as a term in the K_c expression, as discussed earlier, even though it may also appear as a reactant or product in the chemical equation.

Reactions in which all reactants and products are gases represent a second class of homogeneous equilibria. We use molar concentrations in the following examples, but we will see shortly that partial pressures of the gases may be used as well.

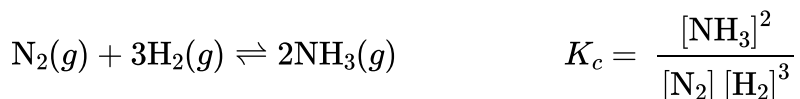
Equation:



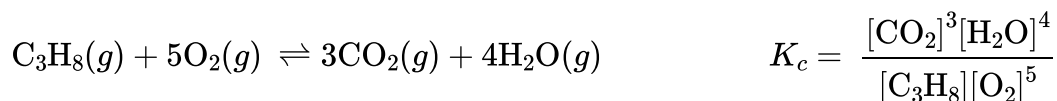
Equation:



Equation:



Equation:



Note that the concentration of $\text{H}_2\text{O}(g)$ has been included in the last example because water is not the solvent in this gas-phase reaction and its concentration (and activity) changes.

Whenever gases are involved in a reaction, the partial pressure of each gas can be used instead of its concentration in the equation for the reaction quotient because the partial pressure of a gas is directly proportional to its concentration at constant temperature. This relationship can be derived from the ideal gas equation, where M is the molar concentration of gas, $\frac{n}{V}$.

Equation:

$$PV = nRT$$

Equation:

$$P = \left(\frac{n}{V}\right)RT$$

Equation:

$$= MRT$$

Thus, at constant temperature, the pressure of a gas is directly proportional to its concentration.

Using the partial pressures of the gases, we can write the reaction quotient for the system $\text{C}_2\text{H}_6(g) \rightleftharpoons \text{C}_2\text{H}_4(g) + \text{H}_2(g)$ by following the same guidelines for deriving concentration-based expressions:

Equation:

$$Q_P = \frac{P_{\text{C}_2\text{H}_4}P_{\text{H}_2}}{P_{\text{C}_2\text{H}_6}}$$

In this equation we use Q_P to indicate a reaction quotient written with partial pressures: $P_{\text{C}_2\text{H}_6}$ is the partial pressure of C_2H_6 ; P_{H_2} , the partial pressure of H_2 ; and $P_{\text{C}_2\text{H}_4}$, the partial pressure of C_2H_4 . At equilibrium:

Equation:

$$K_P = Q_P = \frac{P_{\text{C}_2\text{H}_4}P_{\text{H}_2}}{P_{\text{C}_2\text{H}_6}}$$

The subscript P in the symbol K_P designates an equilibrium constant derived using partial pressures instead of concentrations. The equilibrium constant, K_P , is still a constant, but its numeric value may differ from the equilibrium constant found for the same reaction by using concentrations.

Conversion between a value for K_C , an equilibrium constant expressed in terms of concentrations, and a value for K_P , an equilibrium constant expressed in terms of pressures, is straightforward (a K or Q without a subscript could be either concentration or pressure).

The equation relating K_C and K_P is derived as follows. For the gas-phase reaction $m\text{A} + n\text{B} \rightleftharpoons x\text{C} + y\text{D}$:

Equation:

$$K_P = \frac{(P_C)^x(P_D)^y}{(P_A)^m(P_B)^n}$$

Equation:

$$= \frac{([C] \times RT)^x ([D] \times RT)^y}{([A] \times RT)^m ([B] \times RT)^n}$$

Equation:

$$= \frac{[C]^x [D]^y}{[A]^m [B]^n} \times \frac{(RT)^{x+y}}{(RT)^{m+n}}$$

Equation:

$$= K_c (RT)^{(x+y)-(m+n)}$$

Equation:

$$= K_c (RT)^{\Delta n}$$

The relationship between K_c and K_p is

Equation:

$$K_p = K_c (RT)^{\Delta n}$$

In this equation, Δn is the difference between the sum of the coefficients of the *gaseous* products and the sum of the coefficients of the *gaseous* reactants in the reaction (the change in moles of gas between the reactants and the products). For the gas-phase reaction $mA + nB \rightleftharpoons xC + yD$, we have

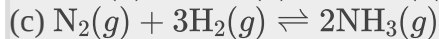
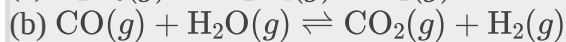
Equation:

$$\Delta n = (x+y) - (m+n)$$

Example:

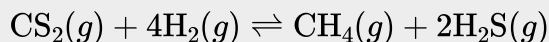
Calculation of K_p

Write the equations for the conversion of K_c to K_p for each of the following reactions:



(d) K_c is equal to 0.28 for the following reaction at 900 °C:

Equation:



What is K_p at this temperature?

Solution

$$(a) \Delta n = (2) - (1) = 1$$

$$K_P = K_c (RT)^{\Delta n} = K_c (RT)^1 = K_c (RT)$$

$$(b) \Delta n = (2) - (2) = 0$$

$$K_P = K_c (RT)^{\Delta n} = K_c (RT)^0 = K_c$$

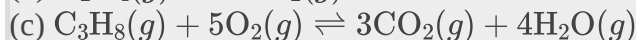
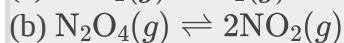
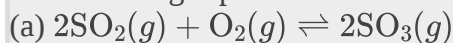
$$(c) \Delta n = (2) - (1 + 3) = -2$$

$$K_P = K_c (RT)^{\Delta n} = K_c (RT)^{-2} = \frac{K_c}{(RT)^2}$$

$$(d) K_P = K_c (RT)^{\Delta n} = (0.28)[(0.0821)(1173)]^{-2} = 3.0 \times 10^{-5}$$

Check Your Learning

Write the equations for the conversion of K_c to K_P for each of the following reactions, which occur in the gas phase:



(d) At 227 °C, the following reaction has $K_c = 0.0952$:

Equation:



What would be the value of K_P at this temperature?

Note:

Answer:

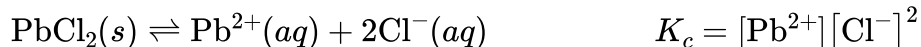
(a) $K_P = K_c (RT)^{-1}$; (b) $K_P = K_c (RT)$; (c) $K_P = K_c (RT)$; (d) 160 or 1.6×10^2

Heterogeneous Equilibria

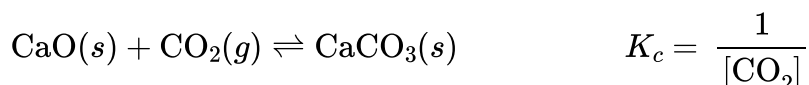
A **heterogeneous equilibrium** is a system in which reactants and products are found in two or more phases. The phases may be any combination of solid, liquid, or gas phases, and solutions. When dealing with these equilibria, remember that solids and pure liquids do not appear in equilibrium constant expressions (the activities of pure solids, pure liquids, and solvents are 1).

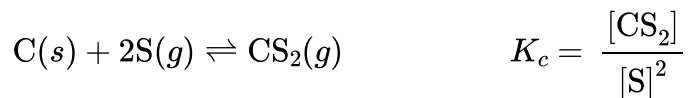
Some heterogeneous equilibria involve chemical changes; for example:

Equation:



Equation:

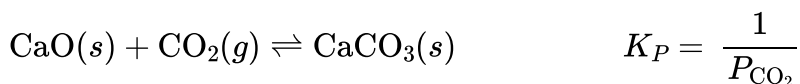
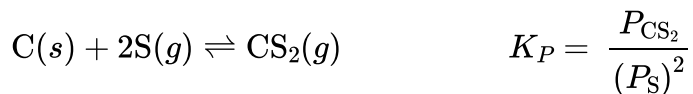


Equation:

Other heterogeneous equilibria involve phase changes, for example, the evaporation of liquid bromine, as shown in the following equation:

Equation:

We can write equations for reaction quotients of heterogeneous equilibria that involve gases, using partial pressures instead of concentrations. Two examples are:

Equation:**Equation:****Key Concepts and Summary**

For any reaction that is at equilibrium, the reaction quotient Q is equal to the equilibrium constant K for the reaction. If a reactant or product is a pure solid, a pure liquid, or the solvent in a dilute solution, the concentration of this component does not appear in the expression for the equilibrium constant. At equilibrium, the values of the concentrations of the reactants and products are constant. Their particular values may vary depending on conditions, but the value of the reaction quotient will always equal K (K_c when using concentrations or K_P when using partial pressures).

A homogeneous equilibrium is an equilibrium in which all components are in the same phase. A heterogeneous equilibrium is an equilibrium in which components are in two or more phases. We can decide whether a reaction is at equilibrium by comparing the reaction quotient with the equilibrium constant for the reaction.

Key Equations

$$\bullet \quad Q = \frac{[\text{C}]^x[\text{D}]^y}{[\text{A}]^m[\text{B}]^n} \qquad \text{where } m\text{A} + n\text{B} \rightleftharpoons x\text{C} + y\text{D}$$

- $Q_P = \frac{(P_C)^x (P_D)^y}{(P_A)^m (P_B)^n}$ where $mA + nB \rightleftharpoons xC + yD$
- $P = MRT$
- $K_P = K_c (RT)^{\Delta n}$

Chemistry End of Chapter Exercises

Exercise:

Problem:

Explain why there may be an infinite number of values for the reaction quotient of a reaction at a given temperature but there can be only one value for the equilibrium constant at that temperature.

Exercise:

Problem:

Explain why an equilibrium between $\text{Br}_2(l)$ and $\text{Br}_2(g)$ would not be established if the container were not a closed vessel shown in [\[link\]](#).

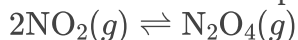
Solution:

Equilibrium cannot be established between the liquid and the gas phase if the top is removed from the bottle because the system is not closed; one of the components of the equilibrium, the Br_2 vapor, would escape from the bottle until all liquid disappeared. Thus, more liquid would evaporate than can condense back from the gas phase to the liquid phase.

Exercise:

Problem:

If you observe the following reaction at equilibrium, is it possible to tell whether the reaction started with pure NO_2 or with pure N_2O_4 ?



Exercise:

Problem:

Among the solubility rules previously discussed is the statement: All chlorides are soluble except Hg_2Cl_2 , AgCl , PbCl_2 , and CuCl .

(a) Write the expression for the equilibrium constant for the reaction represented by the equation $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$. Is $K_c > 1$, < 1 , or ≈ 1 ? Explain your answer.

(b) Write the expression for the equilibrium constant for the reaction represented by the equation $\text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq) \rightleftharpoons \text{PbCl}_2(s)$. Is $K_c > 1$, < 1 , or ≈ 1 ? Explain your answer.

Solution:

(a) $K_c = [\text{Ag}^+][\text{Cl}^-] < 1$. AgCl is insoluble; thus, the concentrations of ions are much less than 1 M ; (b) $K_c = \frac{1}{[\text{Pb}^{2+}][\text{Cl}^-]^2} > 1$ because PbCl_2 is insoluble and formation of the solid will reduce the concentration of ions to a low level ($< 1\text{ M}$).

Exercise:**Problem:**

Among the solubility rules previously discussed is the statement: Carbonates, phosphates, borates, and arsenates—except those of the ammonium ion and the alkali metals—are insoluble.

(a) Write the expression for the equilibrium constant for the reaction represented by the equation $\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq)$. Is $K_c > 1$, < 1 , or ≈ 1 ? Explain your answer.

(b) Write the expression for the equilibrium constant for the reaction represented by the equation $3\text{Ba}^{2+}(aq) + 2\text{PO}_4^{3-}(aq) \rightleftharpoons \text{Ba}_3(\text{PO}_4)_2(s)$. Is $K_c > 1$, < 1 , or ≈ 1 ? Explain your answer.

Exercise:**Problem:**

Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene:

$3\text{C}_2\text{H}_2(g) \longrightarrow \text{C}_6\text{H}_6(g)$. Which value of K_c would make this reaction most useful commercially? $K_c \approx 0.01$, $K_c \approx 1$, or $K_c \approx 10$. Explain your answer.

Solution:

Since $K_c = \frac{[\text{C}_6\text{H}_6]}{[\text{C}_2\text{H}_2]^3}$, a value of $K_c \approx 10$ means that C_6H_6 predominates over C_2H_2 . In such a case, the reaction would be commercially feasible if the rate to equilibrium is suitable.

Exercise:**Problem:**

Show that the complete chemical equation, the total ionic equation, and the net ionic equation for the reaction represented by the equation $\text{KI}(aq) + \text{I}_2(aq) \rightleftharpoons \text{KI}_3(aq)$ give the same expression for the reaction quotient. KI_3 is composed of the ions K^+ and I_3^- .

Exercise:**Problem:**

For a titration to be effective, the reaction must be rapid and the yield of the reaction must essentially be 100%. Is $K_c > 1$, < 1 , or ≈ 1 for a titration reaction?

Solution:

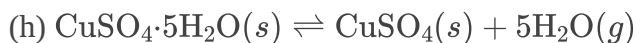
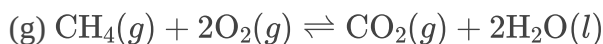
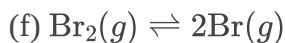
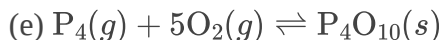
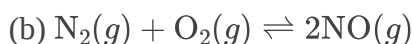
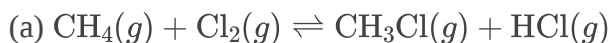
$$K_c > 1$$

Exercise:**Problem:**

For a precipitation reaction to be useful in a gravimetric analysis, the product of the reaction must be insoluble. Is $K_c > 1$, < 1 , or ≈ 1 for a useful precipitation reaction?

Exercise:**Problem:**

Write the mathematical expression for the reaction quotient, Q_c , for each of the following reactions:

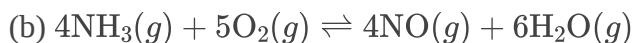
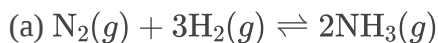


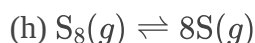
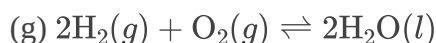
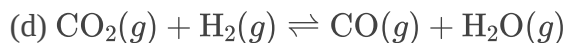
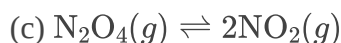
Solution:

$$\begin{aligned} \text{(a)} \quad Q_c &= \frac{[\text{CH}_3\text{Cl}][\text{HCl}]}{[\text{CH}_4][\text{Cl}_2]}; \text{(b)} \quad Q_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}; \text{(c)} \quad Q_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}; \text{(d)} \quad Q_c = [\text{SO}_2]; \text{(e)} \\ Q_c &= \frac{1}{[\text{P}_4][\text{O}_2]^5}; \text{(f)} \quad Q_c = \frac{[\text{Br}]^2}{[\text{Br}_2]}; \text{(g)} \quad Q_c = \frac{[\text{CO}_2]}{[\text{CH}_4][\text{O}_2]^2}; \text{(h)} \quad Q_c = [\text{H}_2\text{O}]^5 \end{aligned}$$

Exercise:**Problem:**

Write the mathematical expression for the reaction quotient, Q_c , for each of the following reactions:

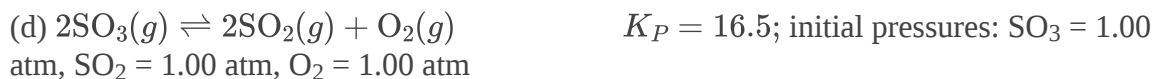
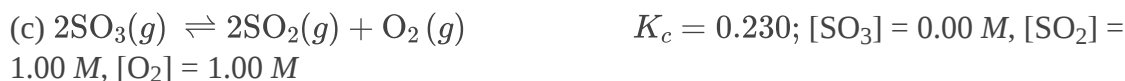




Exercise:

Problem:

The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.



Solution:

(a) $Q_c = 25$ proceeds left; (b) $Q_P = 0.22$ proceeds right; (c) Q_c undefined proceeds left; (d) $Q_P = 1.00$ proceeds right; (e) $Q_P = 0$ proceeds right; (f) $Q_c = 4$ proceeds left

Exercise:

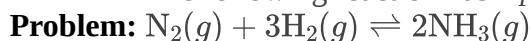
Problem:

The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.

- (a) $2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g)$ $K_c = 17$; $[\text{NH}_3] = 0.50\text{ M}$, $[\text{N}_2] = 0.15\text{ M}$, $[\text{H}_2] = 0.12\text{ M}$
- (b) $2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g)$ $K_P = 6.8 \times 10^4$; initial pressures: $\text{NH}_3 = 2.00\text{ atm}$, $\text{N}_2 = 10.00\text{ atm}$, $\text{H}_2 = 10.00\text{ atm}$
- (c) $2\text{SO}_3(g) \rightleftharpoons 2\text{SO}_2(g) + \text{O}_2(g)$ $K_c = 0.230$; $[\text{SO}_3] = 2.00\text{ M}$, $[\text{SO}_2] = 2.00\text{ M}$, $[\text{O}_2] = 2.00\text{ M}$
- (d) $2\text{SO}_3(g) \rightleftharpoons 2\text{SO}_2(g) + \text{O}_2(g)$ $K_P = 6.5\text{ atm}$; initial pressures: $\text{SO}_2 = 1.00\text{ atm}$, $\text{O}_2 = 1.130\text{ atm}$, $\text{SO}_3 = 0\text{ atm}$
- (e) $2\text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{NOCl}(g)$ $K_P = 2.5 \times 10^3$; initial pressures: $\text{NO} = 1.00\text{ atm}$, $\text{Cl}_2 = 1.00\text{ atm}$, $\text{NOCl} = 0\text{ atm}$
- (f) $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g)$ $K_c = 0.050$; $[\text{N}_2] = 0.100\text{ M}$, $[\text{O}_2] = 0.200\text{ M}$, $[\text{NO}] = 1.00\text{ M}$

Exercise:

The following reaction has $K_P = 4.50 \times 10^{-5}$ at 720 K.



If a reaction vessel is filled with each gas to the partial pressures listed, in which direction will it shift to reach equilibrium? $P(\text{NH}_3) = 93\text{ atm}$, $P(\text{N}_2) = 48\text{ atm}$, and $P(\text{H}_2) = 52$

Solution:

The system will shift toward the reactants to reach equilibrium.

Exercise:

Problem:

Determine if the following system is at equilibrium. If not, in which direction will the system need to shift to reach equilibrium?



$[\text{SO}_2\text{Cl}_2] = 0.12\text{ M}$, $[\text{Cl}_2] = 0.16\text{ M}$ and $[\text{SO}_2] = 0.050\text{ M}$. K_c for the reaction is 0.078.

Exercise:

Problem:

Which of the systems described in [\[link\]](#) give homogeneous equilibria? Which give heterogeneous equilibria?

Solution:

- (a) homogenous; (b) homogenous; (c) homogenous; (d) heterogeneous; (e) heterogeneous;
(f) homogenous; (g) heterogeneous; (h) heterogeneous

Exercise:

Problem:

Which of the systems described in [\[link\]](#) give homogeneous equilibria? Which give heterogeneous equilibria?

Exercise:

Problem:

For which of the reactions in [\[link\]](#) does K_c (calculated using concentrations) equal K_P (calculated using pressures)?

Solution:

This situation occurs in (a) and (b).

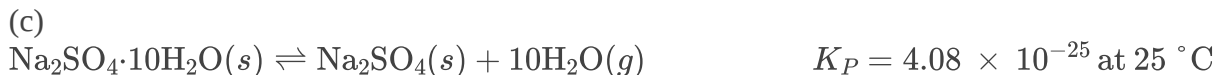
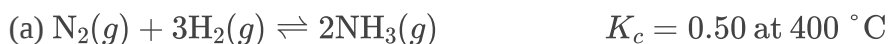
Exercise:

Problem:

For which of the reactions in [\[link\]](#) does K_c (calculated using concentrations) equal K_P (calculated using pressures)?

Exercise:

Problem: Convert the values of K_c to values of K_P or the values of K_P to values of K_c .



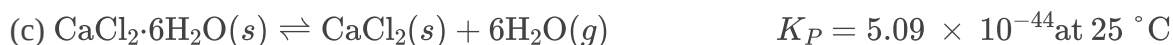
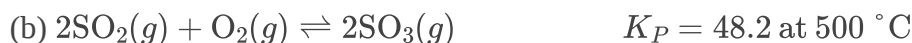
Solution:

(a) $K_P = 1.6 \times 10^{-4}$; (b) $K_P = 50.2$; (c) $K_c = 5.31 \times 10^{-39}$; (d) $K_c = 4.60 \times 10^{-3}$

Exercise:

Problem: Convert the values of K_c to values of K_P or the values of K_P to values of K_c .





Exercise:

Problem:

What is the value of the equilibrium constant expression for the change $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g)$ at 30°C ? (See [Appendix E](#).)

Solution:

$$K_P = P_{\text{H}_2\text{O}} = 0.042.$$

Exercise:

Problem:

Write the expression of the reaction quotient for the ionization of HOCN in water.

Exercise:

Problem: Write the reaction quotient expression for the ionization of NH_3 in water.

Solution:

$$Q_c = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

Exercise:

Problem:

What is the approximate value of the equilibrium constant K_P for the change $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5(l) \rightleftharpoons \text{C}_2\text{H}_5\text{OC}_2\text{H}_5(g)$ at 25°C . (Vapor pressure was described in the previous chapter on liquids and solids; refer back to this chapter to find the relevant information needed to solve this problem.)

Glossary

equilibrium constant (K)

value of the reaction quotient for a system at equilibrium

heterogeneous equilibria

equilibria between reactants and products in different phases

homogeneous equilibria

equilibria within a single phase

K_c

equilibrium constant for reactions based on concentrations of reactants and products

K_p

equilibrium constant for gas-phase reactions based on partial pressures of reactants and products

law of mass action

when a reversible reaction has attained equilibrium at a given temperature, the reaction quotient remains constant

reaction quotient (Q)

ratio of the product of molar concentrations (or pressures) of the products to that of the reactants, each concentration (or pressure) being raised to the power equal to the coefficient in the equation

Shifting Equilibria: Le Châtelier's Principle

By the end of this section, you will be able to:

- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Châtelier's principle

As we saw in the previous section, reactions proceed in both directions (reactants go to products and products go to reactants). We can tell a reaction is at equilibrium if the reaction quotient (Q) is equal to the equilibrium constant (K). We next address what happens when a system at equilibrium is disturbed so that Q is no longer equal to K . If a system at equilibrium is subjected to a perturbation or **stress** (such as a change in concentration) the **position of equilibrium** changes. Since this stress affects the concentrations of the reactants and the products, the value of Q will no longer equal the value of K . To re-establish equilibrium, the system will either shift toward the products (if $Q < K$) or the reactants (if $Q > K$) until Q returns to the same value as K .

This process is described by **Le Châtelier's principle**: When a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance. As described in the previous paragraph, the disturbance causes a change in Q ; the reaction will shift to re-establish $Q = K$.

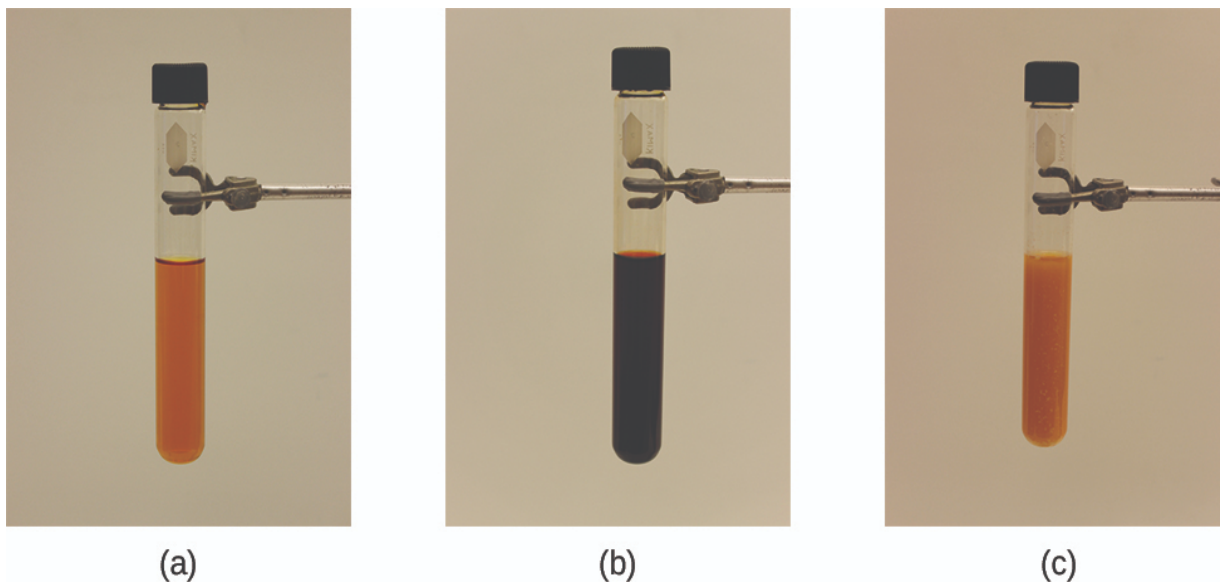
Predicting the Direction of a Reversible Reaction

Le Châtelier's principle can be used to predict changes in equilibrium concentrations when a system that is at equilibrium is subjected to a stress. However, if we have a mixture of reactants and products that have not yet reached equilibrium, the changes necessary to reach equilibrium may not be so obvious. In such a case, we can compare the values of Q and K for the system to predict the changes.

Effect of Change in Concentration on Equilibrium

A chemical system at equilibrium can be temporarily shifted out of equilibrium by adding or removing one or more of the reactants or products. The concentrations of both reactants and products then undergo additional changes to return the system to equilibrium.

The stress on the system in [\[link\]](#) is the reduction of the equilibrium concentration of SCN^- (lowering the concentration of one of the reactants would cause Q to be larger than K). As a consequence, Le Châtelier's principle leads us to predict that the concentration of $\text{Fe}(\text{SCN})^{2+}$ should decrease, increasing the concentration of SCN^- part way back to its original concentration, and increasing the concentration of Fe^{3+} above its initial equilibrium concentration.



(a) The test tube contains 0.1 M Fe^{3+} . (b) Thiocyanate ion has been added to solution in (a), forming the red $\text{Fe}(\text{SCN})^{2+}$ ion.
 $\text{Fe}^{3+}(\text{aq}) + \text{SCN}^{-}(\text{aq}) \rightleftharpoons \text{Fe}(\text{SCN})^{2+}(\text{aq})$. (c) Silver nitrate has been added to the solution in (b), precipitating some of the SCN^{-} as the white solid AgSCN .
 $\text{Ag}^{+}(\text{aq}) + \text{SCN}^{-}(\text{aq}) \rightleftharpoons \text{AgSCN}(\text{s})$. The decrease in the SCN^{-} concentration shifts the first equilibrium in the solution to the left, decreasing the concentration (and lightening color) of the $\text{Fe}(\text{SCN})^{2+}$. (credit: modification of work by Mark Ott)

The effect of a change in concentration on a system at equilibrium is illustrated further by the equilibrium of this chemical reaction:

Equation:



The numeric values for this example have been determined experimentally. A mixture of gases at $400\text{ }^{\circ}\text{C}$ with $[\text{H}_2] = [\text{I}_2] = 0.221\text{ M}$ and $[\text{HI}] = 1.563\text{ M}$ is at equilibrium; for this mixture, $Q_c = K_c = 50.0$. If H_2 is introduced into the system so quickly that its concentration doubles before it begins to react (new $[\text{H}_2] = 0.442\text{ M}$), the reaction will shift so that a new equilibrium is reached, at which $[\text{H}_2] = 0.374\text{ M}$, $[\text{I}_2] = 0.153\text{ M}$, and $[\text{HI}] = 1.692\text{ M}$. This gives:

Equation:

$$Q_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(1.692)^2}{(0.374)(0.153)} = 50.0 = K_c$$

We have stressed this system by introducing additional H_2 . The stress is relieved when the reaction shifts to the right, using up some (but not all) of the excess H_2 , reducing the amount of uncombined I_2 , and forming additional HI .

Effect of Change in Pressure on Equilibrium

Sometimes we can change the position of equilibrium by changing the pressure of a system. However, changes in pressure have a measurable effect only in systems in which gases are involved, and then only when the chemical reaction produces a change in the total number of gas molecules in the system. An easy way to recognize such a system is to look for different numbers of moles of gas on the reactant and product sides of the equilibrium. While evaluating pressure (as well as related factors like volume), it is important to remember that equilibrium constants are defined with regard to concentration (for K_c) or partial pressure (for K_p). Some changes to total pressure, like adding an inert gas that is not part of the equilibrium, will change the total pressure but not the partial pressures of the gases in the equilibrium constant expression. Thus, addition of a gas not involved in the equilibrium will not perturb the equilibrium.

Note:



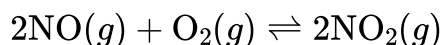
Check out this [link](#) to see a dramatic visual demonstration of how equilibrium changes with pressure changes.

As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of one of the components of the equilibrium mixture, we introduce a stress by increasing the partial pressures of one or more of the components. In accordance with Le Châtelier's principle, a shift in the equilibrium that

reduces the total number of molecules per unit of volume will be favored because this relieves the stress. The reverse reaction would be favored by a decrease in pressure.

Consider what happens when we increase the pressure on a system in which NO, O₂, and NO₂ are at equilibrium:

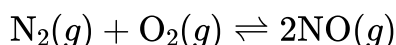
Equation:



The formation of additional amounts of NO₂ decreases the total number of molecules in the system because each time two molecules of NO₂ form, a total of three molecules of NO and O₂ are consumed. This reduces the total pressure exerted by the system and reduces, but does not completely relieve, the stress of the increased pressure. On the other hand, a decrease in the pressure on the system favors decomposition of NO₂ into NO and O₂, which tends to restore the pressure.

Now consider this reaction:

Equation:



Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not favor either formation or decomposition of gaseous nitrogen monoxide.

Effect of Change in Temperature on Equilibrium

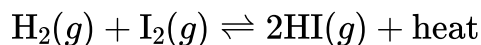
Changing concentration or pressure perturbs an equilibrium because the reaction quotient is shifted away from the equilibrium value. Changing the temperature of a system at equilibrium has a different effect: A change in temperature actually changes the value of the equilibrium constant. However, we can qualitatively predict the effect of the temperature change by treating it as a stress on the system and applying Le Châtelier's principle.

When hydrogen reacts with gaseous iodine, heat is evolved.

Equation:



Because this reaction is exothermic, we can write it with heat as a product.

Equation:

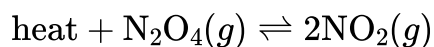
Increasing the temperature of the reaction increases the internal energy of the system. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of H_2 and I_2 and a reduction in the concentration of HI . Lowering the temperature of this system reduces the amount of energy present, favors the production of heat, and favors the formation of hydrogen iodide.

When we change the temperature of a system at equilibrium, the equilibrium constant for the reaction changes. Lowering the temperature in the HI system increases the equilibrium constant: At the new equilibrium the concentration of HI has increased and the concentrations of H_2 and I_2 decreased. Raising the temperature decreases the value of the equilibrium constant, from 67.5 at 357 °C to 50.0 at 400 °C.

Temperature affects the equilibrium between NO_2 and N_2O_4 in this reaction

Equation:

The positive ΔH value tells us that the reaction is endothermic and could be written

Equation:

At higher temperatures, the gas mixture has a deep brown color, indicative of a significant amount of brown NO_2 molecules. If, however, we put a stress on the system by cooling the mixture (withdrawing energy), the equilibrium shifts to the left to supply some of the energy lost by cooling. The concentration of colorless N_2O_4 increases, and the concentration of brown NO_2 decreases, causing the brown color to fade.

Note:



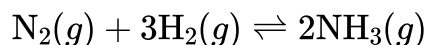
This interactive [animation](#) allows you to apply Le Châtelier's principle to predict the effects of changes in concentration, pressure, and temperature on reactant and product concentrations.

Catalysts Do Not Affect Equilibrium

As we learned during our study of kinetics, a catalyst can speed up the rate of a reaction. Though this increase in reaction rate may cause a system to reach equilibrium more quickly (by speeding up the forward and reverse reactions), a catalyst has no effect on the value of an equilibrium constant nor on equilibrium concentrations.

The interplay of changes in concentration or pressure, temperature, and the lack of an influence of a catalyst on a chemical equilibrium is illustrated in the industrial synthesis of ammonia from nitrogen and hydrogen according to the equation

Equation:



A large quantity of ammonia is manufactured by this reaction. Each year, ammonia is among the top 10 chemicals, by mass, manufactured in the world. About 2 billion pounds are manufactured in the United States each year.

Ammonia plays a vital role in our global economy. It is used in the production of fertilizers and is, itself, an important fertilizer for the growth of corn, cotton, and other crops. Large quantities of ammonia are converted to nitric acid, which plays an important role in the production of fertilizers, explosives, plastics, dyes, and fibers, and is also used in the steel industry.

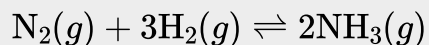
Note:

Fritz Haber

In the early 20th century, German chemist Fritz Haber ([link](#)) developed a practical process for converting diatomic nitrogen, which cannot be used by plants as a nutrient,

to ammonia, a form of nitrogen that is easiest for plants to absorb.

Equation:



The availability of nitrogen is a strong limiting factor to the growth of plants. Despite accounting for 78% of air, diatomic nitrogen (N_2) is nutritionally unavailable due to the tremendous stability of the nitrogen-nitrogen triple bond. For plants to use atmospheric nitrogen, the nitrogen must be converted to a more bioavailable form (this conversion is called nitrogen fixation).

Haber was born in Breslau, Prussia (presently Wroclaw, Poland) in December 1868. He went on to study chemistry and, while at the University of Karlsruhe, he developed what would later be known as the Haber process: the catalytic formation of ammonia from hydrogen and atmospheric nitrogen under high temperatures and pressures. For this work, Haber was awarded the 1918 Nobel Prize in Chemistry for synthesis of ammonia from its elements. The Haber process was a boon to agriculture, as it allowed the production of fertilizers to no longer be dependent on mined feed stocks such as sodium nitrate. Currently, the annual production of synthetic nitrogen fertilizers exceeds 100 million tons and synthetic fertilizer production has increased the number of humans that arable land can support from 1.9 persons per hectare in 1908 to 4.3 in 2008.



The work of Nobel Prize recipient Fritz Haber revolutionized agricultural practices in the early 20th

century. His work also affected wartime strategies, adding chemical weapons to the artillery.

In addition to his work in ammonia production, Haber is also remembered by history as one of the fathers of chemical warfare. During World War I, he played a major role in the development of poisonous gases used for trench warfare. Regarding his role in these developments, Haber said, “During peace time a scientist belongs to the World, but during war time he belongs to his country.”[\[footnote\]](#) Haber defended the use of gas warfare against accusations that it was inhumane, saying that death was death, by whatever means it was inflicted. He stands as an example of the ethical dilemmas that face scientists in times of war and the double-edged nature of the sword of science.

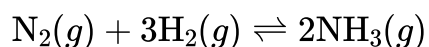
Herrlich, P. “The Responsibility of the Scientist: What Can History Teach Us About How Scientists Should Handle Research That Has the Potential to Create Harm?” *EMBO Reports* 14 (2013): 759–764.

Like Haber, the products made from ammonia can be multifaceted. In addition to their value for agriculture, nitrogen compounds can also be used to achieve destructive ends. Ammonium nitrate has also been used in explosives, including improvised explosive devices. Ammonium nitrate was one of the components of the bomb used in the attack on the Alfred P. Murrah Federal Building in downtown Oklahoma City on April 19, 1995.

It has long been known that nitrogen and hydrogen react to form ammonia. However, it became possible to manufacture ammonia in useful quantities by the reaction of nitrogen and hydrogen only in the early 20th century after the factors that influence its equilibrium were understood.

To be practical, an industrial process must give a large yield of product relatively quickly. One way to increase the yield of ammonia is to increase the pressure on the system in which N_2 , H_2 , and NH_3 are at equilibrium or are coming to equilibrium.

Equation:

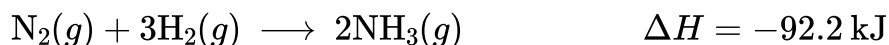


The formation of additional amounts of ammonia reduces the total pressure exerted by the system and somewhat reduces the stress of the increased pressure.

Although increasing the pressure of a mixture of N_2 , H_2 , and NH_3 will increase the yield of ammonia, at low temperatures, the rate of formation of ammonia is slow. At room

temperature, for example, the reaction is so slow that if we prepared a mixture of N_2 and H_2 , no detectable amount of ammonia would form during our lifetime. The formation of ammonia from hydrogen and nitrogen is an exothermic process:

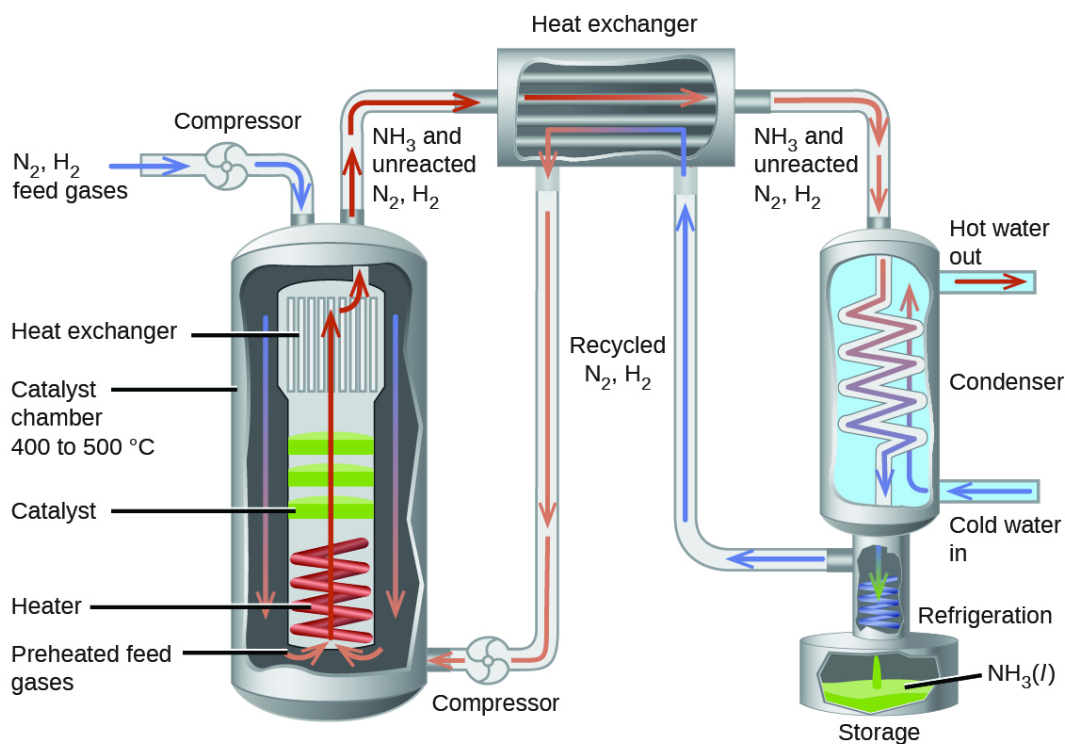
Equation:



Thus, increasing the temperature to increase the rate lowers the yield. If we lower the temperature to shift the equilibrium to favor the formation of more ammonia, equilibrium is reached more slowly because of the large decrease of reaction rate with decreasing temperature.

Part of the rate of formation lost by operating at lower temperatures can be recovered by using a catalyst. The net effect of the catalyst on the reaction is to cause equilibrium to be reached more rapidly.

In the commercial production of ammonia, conditions of about 500°C , 150–900 atm, and the presence of a catalyst are used to give the best compromise among rate, yield, and the cost of the equipment necessary to produce and contain high-pressure gases at high temperatures ([link](#)).



Commercial production of ammonia requires heavy equipment to handle the high temperatures and pressures required. This schematic outlines the design of an ammonia plant.

Key Concepts and Summary

Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure; volume and pressure changes will disturb equilibrium if the number of moles of gas is different on the reactant and product sides of the reaction. The system's response to these disturbances is described by Le Châtelier's principle: The system will respond in a way that counteracts the disturbance. Not all changes to the system result in a disturbance of the equilibrium. Adding a catalyst affects the rates of the reactions but does not alter the equilibrium, and changing pressure or volume will not significantly disturb systems with no gases or with equal numbers of moles of gas on the reactant and product side.

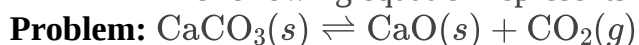
Effects of Disturbances of Equilibrium and K			
Disturbance	Observed Change as Equilibrium is Restored	Direction of Shift	Effect on K
reactant added	added reactant is partially consumed	toward products	none
product added	added product is partially consumed	toward reactants	none
decrease in volume/increase in gas pressure	pressure decreases	toward side with fewer moles of gas	none

Effects of Disturbances of Equilibrium and K			
Disturbance	Observed Change as Equilibrium is Restored	Direction of Shift	Effect on K
increase in volume/decrease in gas pressure	pressure increases	toward side with more moles of gas	none
temperature increase	heat is absorbed	toward products for endothermic, toward reactants for exothermic	changes
temperature decrease	heat is given off	toward reactants for endothermic, toward products for exothermic	changes

Chemistry End of Chapter Exercises

Exercise:

The following equation represents a reversible decomposition:



Under what conditions will decomposition in a closed container proceed to completion so that no CaCO_3 remains?

Solution:

The amount of CaCO_3 must be so small that P_{CO_2} is less than K_P when the CaCO_3 has completely decomposed. In other words, the starting amount of CaCO_3 cannot completely generate the full P_{CO_2} required for equilibrium.

Exercise:

Problem:

Explain how to recognize the conditions under which changes in pressure would affect systems at equilibrium.

Exercise:**Problem:**

What property of a reaction can we use to predict the effect of a change in temperature on the value of an equilibrium constant?

Solution:

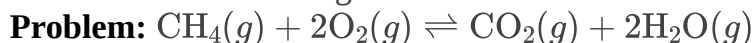
The change in enthalpy may be used. If the reaction is exothermic, the heat produced can be thought of as a product. If the reaction is endothermic the heat added can be thought of as a reactant. Additional heat would shift an exothermic reaction back to the reactants but would shift an endothermic reaction to the products. Cooling an exothermic reaction causes the reaction to shift toward the product side; cooling an endothermic reaction would cause it to shift to the reactants' side.

Exercise:**Problem:**

What would happen to the color of the solution in part (b) of [\[link\]](#) if a small amount of NaOH were added and $\text{Fe}(\text{OH})_3$ precipitated? Explain your answer.

Exercise:

The following reaction occurs when a burner on a gas stove is lit:



Is an equilibrium among CH_4 , O_2 , CO_2 , and H_2O established under these conditions? Explain your answer.

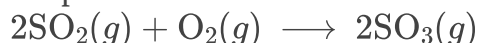
Solution:

No, it is not at equilibrium. Because the system is not confined, products continuously escape from the region of the flame; reactants are also added continuously from the burner and surrounding atmosphere.

Exercise:

Problem:

A necessary step in the manufacture of sulfuric acid is the formation of sulfur trioxide, SO_3 , from sulfur dioxide, SO_2 , and oxygen, O_2 , shown here. At high temperatures, the rate of formation of SO_3 is higher, but the equilibrium amount (concentration or partial pressure) of SO_3 is lower than it would be at lower temperatures.

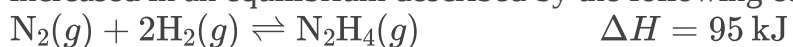


(a) Does the equilibrium constant for the reaction increase, decrease, or remain about the same as the temperature increases?

(b) Is the reaction endothermic or exothermic?

Exercise:**Problem:**

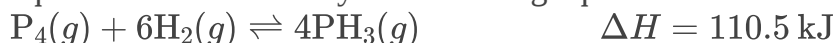
Suggest four ways in which the concentration of hydrazine, N_2H_4 , could be increased in an equilibrium described by the following equation:

**Solution:**

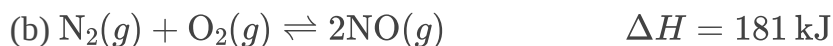
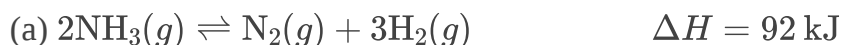
Add N_2 ; add H_2 ; decrease the container volume; heat the mixture.

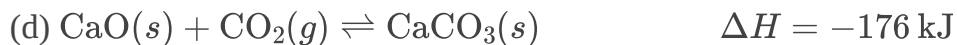
Exercise:**Problem:**

Suggest four ways in which the concentration of PH_3 could be increased in an equilibrium described by the following equation:

**Exercise:****Problem:**

How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?





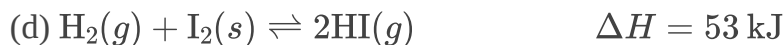
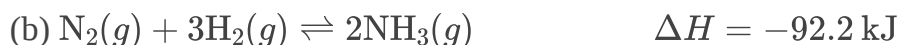
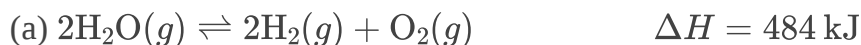
Solution:

(a) ΔT increase = shift right, ΔP increase = shift left; (b) ΔT increase = shift right, ΔP increase = no effect; (c) ΔT increase = shift left, ΔP increase = shift left; (d) ΔT increase = shift left, ΔP increase = shift right.

Exercise:

Problem:

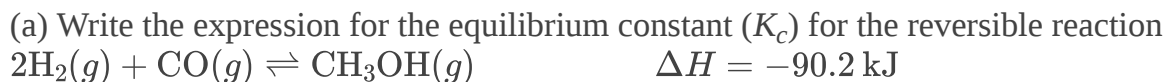
How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?



Exercise:

Problem:

Water gas is a 1:1 mixture of carbon monoxide and hydrogen gas and is called water gas because it is formed from steam and hot carbon in the following reaction: $\text{H}_2\text{O}(g) + \text{C}(s) \rightleftharpoons \text{H}_2(g) + \text{CO}(g)$. Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and hydrogen at high temperature and pressure in the presence of a suitable catalyst.



(b) What will happen to the concentrations of H_2 , CO , and CH_3OH at equilibrium if more H_2 is added?

(c) What will happen to the concentrations of H_2 , CO , and CH_3OH at equilibrium if CO is removed?

(d) What will happen to the concentrations of H_2 , CO , and CH_3OH at equilibrium if CH_3OH is added?

(e) What will happen to the concentrations of H_2 , CO , and CH_3OH at equilibrium if the temperature of the system is increased?

(f) What will happen to the concentrations of H_2 , CO , and CH_3OH at equilibrium if more catalyst is added?

Solution:

(a) $K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{H}_2]^2[\text{CO}]}$; (b) $[\text{H}_2]$ increases, $[\text{CO}]$ decreases, $[\text{CH}_3\text{OH}]$ increases; (c), $[\text{H}_2]$ increases, $[\text{CO}]$ decreases, $[\text{CH}_3\text{OH}]$ decreases; (d), $[\text{H}_2]$ increases, $[\text{CO}]$ increases, $[\text{CH}_3\text{OH}]$ increases; (e), $[\text{H}_2]$ increases, $[\text{CO}]$ increases, $[\text{CH}_3\text{OH}]$ decreases; (f), no changes.

Exercise:

Problem: Nitrogen and oxygen react at high temperatures.

(a) Write the expression for the equilibrium constant (K_c) for the reversible reaction
 $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g) \quad \Delta H = 181 \text{ kJ}$

(b) What will happen to the concentrations of N_2 , O_2 , and NO at equilibrium if more O_2 is added?

(c) What will happen to the concentrations of N_2 , O_2 , and NO at equilibrium if N_2 is removed?

(d) What will happen to the concentrations of N_2 , O_2 , and NO at equilibrium if NO is added?

(e) What will happen to the concentrations of N_2 , O_2 , and NO at equilibrium if the pressure on the system is increased by reducing the volume of the reaction vessel?

(f) What will happen to the concentrations of N_2 , O_2 , and NO at equilibrium if the temperature of the system is increased?

(g) What will happen to the concentrations of N_2 , O_2 , and NO at equilibrium if a catalyst is added?

Exercise:

Problem:

Water gas, a mixture of H_2 and CO , is an important industrial fuel produced by the reaction of steam with red hot coke, essentially pure carbon.

(a) Write the expression for the equilibrium constant for the reversible reaction
 $\text{C}(s) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + \text{H}_2(g) \quad \Delta H = 131.30 \text{ kJ}$

(b) What will happen to the concentration of each reactant and product at equilibrium if more C is added?

(c) What will happen to the concentration of each reactant and product at equilibrium if H₂O is removed?

(d) What will happen to the concentration of each reactant and product at equilibrium if CO is added?

(e) What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

Solution:

(a) $K_c = \frac{[\text{CO}][\text{H}_2]}{[\text{H}_2\text{O}]}$; (b) [H₂O] no change, [CO] no change, [H₂] no change; (c) [H₂O] decreases, [CO] decreases, [H₂] decreases; (d) [H₂O] increases, [CO] increases, [H₂] decreases; (f) [H₂O] decreases, [CO] increases, [H₂] increases. In (b), (c), (d), and (e), the mass of carbon will change, but its concentration (activity) will not change.

Exercise:

Problem:

Pure iron metal can be produced by the reduction of iron(III) oxide with hydrogen gas.

(a) Write the expression for the equilibrium constant (K_c) for the reversible reaction
$$\text{Fe}_2\text{O}_3(s) + 3\text{H}_2(g) \rightleftharpoons 2\text{Fe}(s) + 3\text{H}_2\text{O}(g) \quad \Delta H = 98.7 \text{ kJ}$$

(b) What will happen to the concentration of each reactant and product at equilibrium if more Fe is added?

(c) What will happen to the concentration of each reactant and product at equilibrium if H₂O is removed?

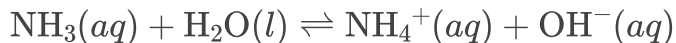
(d) What will happen to the concentration of each reactant and product at equilibrium if H₂ is added?

(e) What will happen to the concentration of each reactant and product at equilibrium if the pressure on the system is increased by reducing the volume of the reaction vessel?

(f) What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

Exercise:**Problem:**

Ammonia is a weak base that reacts with water according to this equation:



Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water?

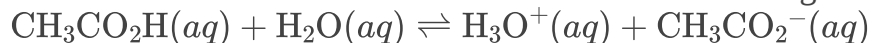
- (a) Addition of NaOH
 - (b) Addition of HCl
 - (c) Addition of NH_4Cl
-

Solution:

Only (b)

Exercise:**Problem:**

Acetic acid is a weak acid that reacts with water according to this equation:

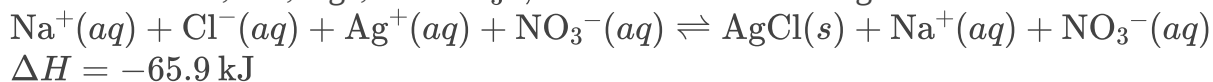


Will any of the following increase the percent of acetic acid that reacts and produces CH_3CO_2^- ion?

- (a) Addition of HCl
- (b) Addition of NaOH
- (c) Addition of NaCH_3CO_2

Exercise:**Problem:**

Suggest two ways in which the equilibrium concentration of Ag^+ can be reduced in a solution of Na^+ , Cl^- , Ag^+ , and NO_3^- , in contact with solid AgCl.

**Solution:**

Add NaCl or some other salt that produces Cl^- to the solution. Cooling the solution forces the equilibrium to the right, precipitating more AgCl(s) .

Exercise:

Problem:

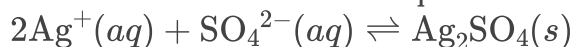
How can the pressure of water vapor be increased in the following equilibrium?



Exercise:

Problem:

Additional solid silver sulfate, a slightly soluble solid, is added to a solution of silver ion and sulfate ion at equilibrium with solid silver sulfate.



Which of the following will occur?

- (a) Ag^+ or SO_4^{2-} concentrations will not change.
 - (b) The added silver sulfate will dissolve.
 - (c) Additional silver sulfate will form and precipitate from solution as Ag^+ ions and SO_4^{2-} ions combine.
 - (d) The Ag^+ ion concentration will increase and the SO_4^{2-} ion concentration will decrease.
-

Solution:

- (a)

Exercise:

Problem:

The amino acid alanine has two isomers, α -alanine and β -alanine. When equal masses of these two compounds are dissolved in equal amounts of a solvent, the solution of α -alanine freezes at the lowest temperature. Which form, α -alanine or β -alanine, has the larger equilibrium constant for ionization ($\text{HX} \rightleftharpoons \text{H}^+ + \text{X}^-$)?

Glossary

Le Châtelier's principle

when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

position of equilibrium

concentrations or partial pressures of components of a reaction at equilibrium
(commonly used to describe conditions before a disturbance)

stress

change to a reaction's conditions that may cause a shift in the equilibrium

Equilibrium Calculations

By the end of this section, you will be able to:

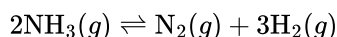
- Write equations representing changes in concentration and pressure for chemical species in equilibrium systems
- Use algebra to perform various types of equilibrium calculations

We know that at equilibrium, the value of the reaction quotient of any reaction is equal to its equilibrium constant. Thus, we can use the mathematical expression for Q to determine a number of quantities associated with a reaction at equilibrium or approaching equilibrium. While we have learned to identify in which direction a reaction will shift to reach equilibrium, we want to extend that understanding to quantitative calculations. We do so by evaluating the ways that the concentrations of products and reactants change as a reaction approaches equilibrium, keeping in mind the stoichiometric ratios of the reaction. This algebraic approach to equilibrium calculations will be explored in this section.

Changes in concentrations or pressures of reactants and products occur as a reaction system approaches equilibrium. In this section we will see that we can relate these changes to each other using the coefficients in the balanced chemical equation describing the system. We use the decomposition of ammonia as an example.

On heating, ammonia reversibly decomposes into nitrogen and hydrogen according to this equation:

Equation:



If a sample of ammonia decomposes in a closed system and the concentration of N_2 increases by 0.11 M , the change in the N_2 concentration, $\Delta[\text{N}_2]$, the final concentration minus the initial concentration, is 0.11 M . The change is positive because the concentration of N_2 increases.

The change in the H_2 concentration, $\Delta[\text{H}_2]$, is also positive—the concentration of H_2 increases as ammonia decomposes. The chemical equation tells us that the change in the concentration of H_2 is three times the change in the concentration of N_2 because for each mole of N_2 produced, 3 moles of H_2 are produced.

Equation:

$$\Delta[\text{H}_2] = 3 \times \Delta[\text{N}_2]$$

Equation:

$$= 3 \times (0.11\text{ M}) = 0.33\text{ M}$$

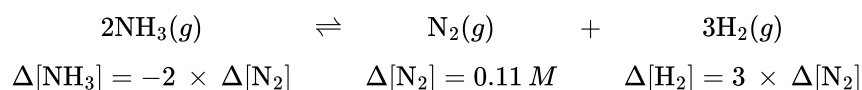
The change in concentration of NH_3 , $\Delta[\text{NH}_3]$, is twice that of $\Delta[\text{N}_2]$; the equation indicates that 2 moles of NH_3 must decompose for each mole of N_2 formed. However, the change in the NH_3 concentration is negative because the concentration of ammonia *decreases* as it decomposes.

Equation:

$$\Delta[\text{NH}_3] = -2 \times \Delta[\text{N}_2] = -2 \times (0.11\text{ M}) = -0.22\text{ M}$$

We can relate these relationships directly to the coefficients in the equation

Equation:



Note that all the changes on one side of the arrows are of the same sign and that all the changes on the other side of the arrows are of the opposite sign.

If we did not know the magnitude of the change in the concentration of N_2 , we could represent it by the symbol x .

Equation:

$$\Delta [\text{N}_2] = x$$

The changes in the other concentrations would then be represented as:

Equation:

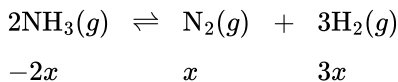
$$\Delta [\text{H}_2] = 3 \times \Delta [\text{N}_2] = 3x$$

Equation:

$$\Delta [\text{NH}_3] = -2 \times \Delta [\text{N}_2] = -2x$$

The coefficients in the Δ terms are identical to those in the balanced equation for the reaction.

Equation:



The simplest way for us to find the coefficients for the concentration changes in any reaction is to use the coefficients in the balanced chemical equation. The sign of the coefficient is positive when the concentration increases; it is negative when the concentration decreases.

Example:

Determining Relative Changes in Concentration

Complete the changes in concentrations for each of the following reactions.

- (a) $\text{C}_2\text{H}_2(g) + 2\text{Br}_2(g) \rightleftharpoons \text{C}_2\text{H}_2\text{Br}_4(g)$
 $\begin{array}{ccccccc} & & & & & & \\ & & & & & & \\ x & & & & & & \end{array}$
- (b) $\text{I}_2(aq) + \text{I}^-(aq) \rightleftharpoons \text{I}_3^-(aq)$
 $\begin{array}{ccccccc} & & & & & & \\ & & & & & & \\ & & & & & & \end{array}$
- (c) $\text{C}_3\text{H}_8(g) + 5\text{O}_2(g) \rightleftharpoons 3\text{CO}_2(g) + 4\text{H}_2\text{O}(g)$
 $\begin{array}{ccccccc} & & & & & & \\ & & & & & & \\ x & & & & & & \end{array}$

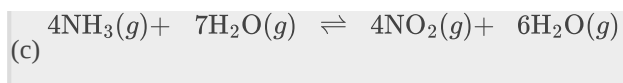
Solution

- (a) $\text{C}_2\text{H}_2(g) + 2\text{Br}_2(g) \rightleftharpoons \text{C}_2\text{H}_2\text{Br}_4(g)$
 $\begin{array}{ccccccc} & & & & & & \\ & & & & & & \\ x & & 2x & & & & -x \end{array}$
- (b) $\text{I}_2(aq) + \text{I}^-(aq) \rightleftharpoons \text{I}_3^-(aq)$
 $\begin{array}{ccccccc} & & & & & & \\ & & & & & & \\ -x & & -x & & & & x \end{array}$
- (c) $\text{C}_3\text{H}_8(g) + 5\text{O}_2(g) \rightleftharpoons 3\text{CO}_2(g) + 4\text{H}_2\text{O}(g)$
 $\begin{array}{ccccccc} & & & & & & \\ & & & & & & \\ x & & 5x & & -3x & & -4x \end{array}$

Check Your Learning

Complete the changes in concentrations for each of the following reactions:

- (a) $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$
 $\begin{array}{ccccccc} & & & & & & \\ & & & & & & \\ & & & & & & \end{array}$
- (b) $\text{C}_4\text{H}_8(g) \rightleftharpoons 2\text{C}_2\text{H}_4(g)$
 $\begin{array}{ccccccc} & & & & & & \\ & & & & & & \\ & & & & & & \end{array}$



Note:

Answer:

(a) $2x, x, -2x$; (b) $x, -2x$; (c) $4x, 7x, -4x, -6x$ or $-4x, -7x, 4x, 6x$

Calculations Involving Equilibrium Concentrations

Because the value of the reaction quotient of any reaction at equilibrium is equal to its equilibrium constant, we can use the mathematical expression for Q_c (i.e., *the law of mass action*) to determine a number of quantities associated with a reaction at equilibrium. It may help if we keep in mind that $Q_c = K_c$ (at equilibrium) in all of these situations and that there are only three basic types of calculations:

1. **Calculation of an equilibrium constant.** If concentrations of reactants and products at equilibrium are known, the value of the equilibrium constant for the reaction can be calculated.
2. **Calculation of missing equilibrium concentrations.** If the value of the equilibrium constant and all of the equilibrium concentrations, except one, are known, the remaining concentration can be calculated.
3. **Calculation of equilibrium concentrations from initial concentrations.** If the value of the equilibrium constant and a set of concentrations of reactants and products that are not at equilibrium are known, the concentrations at equilibrium can be calculated.

A similar list could be generated using Q_p , K_p , and partial pressure. We will look at solving each of these cases in sequence.

Calculation of an Equilibrium Constant

In order to calculate an equilibrium constant, enough information must be available to determine the equilibrium concentrations of all reactants and products. Armed with the concentrations, we can solve the equation for K_c , as it will be the only unknown.

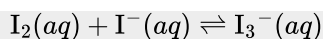
[\[link\]](#) showed us how to determine the equilibrium constant of a reaction if we know the concentrations of reactants and products at equilibrium. The following example shows how to use the stoichiometry of the reaction and a combination of initial concentrations and equilibrium concentrations to determine an equilibrium constant. This technique, commonly called an ICE chart—for Initial, Change, and Equilibrium—will be helpful in solving many equilibrium problems. A chart is generated beginning with the equilibrium reaction in question. The initial concentrations of the reactants and products are provided in the first row of the ICE table (these essentially time-zero concentrations that assume no reaction has taken place). The next row of the table contains the changes in concentrations that result when the reaction proceeds toward equilibrium (don't forget to account for the reaction stoichiometry). The last row contains the concentrations once equilibrium has been reached.

Example:

Calculation of an Equilibrium Constant

Iodine molecules react reversibly with iodide ions to produce triiodide ions.

Equation:



If a solution with the concentrations of I_2 and I^- both equal to $1.000 \times 10^{-3} M$ before reaction gives an equilibrium concentration of I_2 of $6.61 \times 10^{-4} M$, what is the equilibrium constant for the reaction?

Solution

We will begin this problem by calculating the changes in concentration as the system goes to equilibrium. Then we determine the equilibrium concentrations and, finally, the equilibrium constant. First, we set up a table with the initial concentrations, the changes in concentrations, and the equilibrium concentrations using $-x$ as the change in concentration of I_2 .

	I_2	+	I^-	\rightleftharpoons	I_3^-
Initial concentration (M)	1.000×10^{-3}		1.000×10^{-3}		0
Change (M)	$-x$		$-x$		$+x$
Equilibrium concentration (M)	$1.000 \times 10^{-3} - x$		$1.000 \times 10^{-3} - x$		x

Since the equilibrium concentration of I_2 is given, we can solve for x . At equilibrium the concentration of I_2 is $6.61 \times 10^{-4} M$ so that

Equation:

$$1.000 \times 10^{-3} - x = 6.61 \times 10^{-4}$$

Equation:

$$x = 1.000 \times 10^{-3} - 6.61 \times 10^{-4}$$

Equation:

$$= 3.39 \times 10^{-4} M$$

Now we can fill in the table with the concentrations at equilibrium.

	I_2	+	I^-	\rightleftharpoons	I_3^-
Initial concentration (M)	1.000×10^{-3}		1.000×10^{-3}		0
Change (M)	$-x = -3.39 \times 10^{-4}$		$-x$		$+x$
Equilibrium concentration (M)	6.61×10^{-4}		6.61×10^{-4}		3.39×10^{-4}

We now calculate the value of the equilibrium constant.

Equation:

$$K_c = Q_c = \frac{[\text{I}_3^-]}{[\text{I}_2][\text{I}^-]}$$

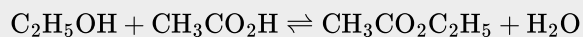
Equation:

$$= \frac{3.39 \times 10^{-4} M}{(6.61 \times 10^{-4} M)(6.61 \times 10^{-4} M)} = 776$$

Check Your Learning

Ethanol and acetic acid react and form water and ethyl acetate, the solvent responsible for the odor of some nail polish removers.

Equation:



When 1 mol each of $\text{C}_2\text{H}_5\text{OH}$ and $\text{CH}_3\text{CO}_2\text{H}$ are allowed to react in 1 L of the solvent dioxane, equilibrium is established when $\frac{1}{3}$ mol of each of the reactants remains. Calculate the equilibrium constant for the reaction. (Note: Water is not a solvent in this reaction.)

Note:

Answer:

$$K_c = 4$$

Calculation of a Missing Equilibrium Concentration

If we know the equilibrium constant for a reaction and know the concentrations at equilibrium of all reactants and products except one, we can calculate the missing concentration.

Example:

Calculation of a Missing Equilibrium Concentration

Nitrogen oxides are air pollutants produced by the reaction of nitrogen and oxygen at high temperatures. At 2000 °C, the value of the equilibrium constant for the reaction, $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g)$, is 4.1×10^{-4} . Calculate the equilibrium concentration of $\text{NO}(g)$ in air at 1 atm pressure and 2000 °C. The equilibrium concentrations of N_2 and O_2 at this pressure and temperature are 0.036 M and 0.0089 M, respectively.

Solution

We are given all of the equilibrium concentrations except that of NO . Thus, we can solve for the missing equilibrium concentration by rearranging the equation for the equilibrium constant.

Equation:

$$K_c = Q_c = \frac{[\text{NO}]^2}{[\text{N}_2] [\text{O}_2]}$$

Equation:

$$[\text{NO}]^2 = K_c [\text{N}_2] [\text{O}_2]$$

Equation:

$$[\text{NO}] = \sqrt{K_c [\text{N}_2] [\text{O}_2]}$$

Equation:

$$= \sqrt{(4.1 \times 10^{-4})(0.036)(0.0089)}$$

Equation:

$$= \sqrt{1.31 \times 10^{-7}}$$

Equation:

$$= 3.6 \times 10^{-4}$$

Thus [NO] is 3.6×10^{-4} mol/L at equilibrium under these conditions.

We can check our answer by substituting all equilibrium concentrations into the expression for the reaction quotient to see whether it is equal to the equilibrium constant.

Equation:

$$Q_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$

Equation:

$$= \frac{(3.6 \times 10^{-4})^2}{(0.036)(0.0089)}$$

Equation:

$$Q_c = 4.0 \times 10^{-4} = K_c$$

The answer checks; our calculated value gives the equilibrium constant within the error associated with the significant figures in the problem.

Check Your Learning

The equilibrium constant for the reaction of nitrogen and hydrogen to produce ammonia at a certain temperature is 6.00×10^{-2} . Calculate the equilibrium concentration of ammonia if the equilibrium concentrations of nitrogen and hydrogen are 4.26 M and 2.09 M, respectively.

Note:

Answer:

1.53 mol/L

Calculation of Equilibrium Concentrations from Initial Concentrations

If we know the equilibrium constant for a reaction and a set of concentrations of reactants and products that are *not at equilibrium*, we can calculate the changes in concentrations as the system comes to equilibrium, as well as the new concentrations at equilibrium. The typical procedure can be summarized in four steps.

1. Determine the direction the reaction proceeds to come to equilibrium.
 - a. Write a balanced chemical equation for the reaction.
 - b. If the direction in which the reaction must proceed to reach equilibrium is not obvious, calculate Q_c from the initial concentrations and compare to K_c to determine the direction of change.

2. Determine the relative changes needed to reach equilibrium, then write the equilibrium concentrations in terms of these changes.
 - a. Define the changes in the initial concentrations that are needed for the reaction to reach equilibrium. Generally, we represent the smallest change with the symbol x and express the other changes in terms of the smallest change.
 - b. Define missing equilibrium concentrations in terms of the initial concentrations and the changes in concentration determined in (a).
3. Solve for the change and the equilibrium concentrations.
 - a. Substitute the equilibrium concentrations into the expression for the equilibrium constant, solve for x , and check any assumptions used to find x .
 - b. Calculate the equilibrium concentrations.
4. Check the arithmetic.
 - a. Check the calculated equilibrium concentrations by substituting them into the equilibrium expression and determining whether they give the equilibrium constant. Sometimes a particular step may differ from problem to problem—it may be more complex in some problems and less complex in others. However, every calculation of equilibrium concentrations from a set of initial concentrations will involve these steps. In solving equilibrium problems that involve changes in concentration, sometimes it is convenient to set up an ICE table, as described in the previous section.

Example:

Calculation of Concentration Changes as a Reaction Goes to Equilibrium

Under certain conditions, the equilibrium constant for the decomposition of $\text{PCl}_5(g)$ into $\text{PCl}_3(g)$ and $\text{Cl}_2(g)$ is 0.0211. What are the equilibrium concentrations of PCl_5 , PCl_3 , and Cl_2 if the initial concentration of PCl_5 was 1.00 M?

Solution

Use the stepwise process described earlier.

<i>Determine the direction the reaction proceeds.</i>	The balanced equation for the decomposition of PCl_5 is	Equation: $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$	Because we have no products initially, $Q_c = 0$ and the reaction will proceed to the right.																
<i>Determine the relative changes needed to reach equilibrium, then write the equilibrium concentrations in terms of these changes.</i>	Let us represent the increase in concentration of PCl_3 by the symbol x . The other changes may be written in terms of x by considering the coefficients in the chemical equation.	Equation: $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$ <div style="display: flex; justify-content: space-around; width: 100%;"> $-x$ x x </div>	The changes in concentration and the expressions for the equilibrium concentrations are: <table border="1" style="margin-top: 10px; width: 100%; border-collapse: collapse; text-align: center;"> <thead> <tr> <th></th> <th>PCl_5</th> <th>PCl_3</th> <th>Cl_2</th> </tr> </thead> <tbody> <tr> <td>Initial concentration (M)</td> <td>1.00</td> <td>0</td> <td>0</td> </tr> <tr> <td>Change (M)</td> <td>$-x$</td> <td>$+x$</td> <td>$+x$</td> </tr> <tr> <td>Equilibrium concentration (M)</td> <td>$1.00 - x$</td> <td>$0 + x = x$</td> <td>$0 + x = x$</td> </tr> </tbody> </table>		PCl_5	PCl_3	Cl_2	Initial concentration (M)	1.00	0	0	Change (M)	$-x$	$+x$	$+x$	Equilibrium concentration (M)	$1.00 - x$	$0 + x = x$	$0 + x = x$
	PCl_5	PCl_3	Cl_2																
Initial concentration (M)	1.00	0	0																
Change (M)	$-x$	$+x$	$+x$																
Equilibrium concentration (M)	$1.00 - x$	$0 + x = x$	$0 + x = x$																
<i>Solve for the change and the equilibrium concentrations.</i>	Substituting the equilibrium concentrations into the equilibrium	Equation: $K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = 0.0211 = \frac{(x)(x)}{(1.00 - x)}$	This equation contains only one variable, x , the change in concentration. Equation: $0.0211 = \frac{(x)(x)}{(1.00 - x)}$																

constant
equation gives

We can write
the equation
as a quadratic
equation and
solve for x
using the
quadratic
formula.

Equation:

Check the Substitution
arithmetic into the
expression
for K_c (to
check the
calculation)
gives

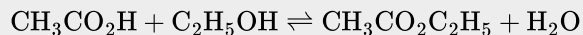
$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{(0.135)(0.135)}{0.87} = 0.021$$

The equilibrium constant calculated
from the equilibrium concentrations is
equal to the value of K_c given in the
problem (when rounded to the proper
number of significant figures). Thus,
the calculated equilibrium
concentrations check.

Check Your Learning

Acetic acid, $\text{CH}_3\text{CO}_2\text{H}$, reacts with ethanol, $\text{C}_2\text{H}_5\text{OH}$, to form water and ethyl acetate, $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$.

Equation:



The equilibrium constant for this reaction with dioxane as a solvent is 4.0. What are the equilibrium concentrations when a mixture that is 0.15 M in $\text{CH}_3\text{CO}_2\text{H}$, 0.15 M in $\text{C}_2\text{H}_5\text{OH}$, 0.40 M in $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$, and 0.40 M in H_2O are mixed in enough dioxane to make 1.0 L of solution?

Note:

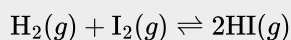
Answer:

$[\text{CH}_3\text{CO}_2\text{H}] = 0.36 \text{ M}$, $[\text{C}_2\text{H}_5\text{OH}] = 0.36 \text{ M}$, $[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5] = 0.17 \text{ M}$, $[\text{H}_2\text{O}] = 0.17 \text{ M}$

Check Your Learning

A 1.00-L flask is filled with 1.00 moles of H_2 and 2.00 moles of I_2 . The value of the equilibrium constant for the reaction of hydrogen and iodine reacting to form hydrogen iodide is 50.5 under the given conditions. What are the equilibrium concentrations of H_2 , I_2 , and HI in moles/L?

Equation:



Note:

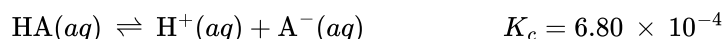
Answer:

$[\text{H}_2] = 0.06\text{ M}$, $[\text{I}_2] = 1.06\text{ M}$, $[\text{HI}] = 1.88\text{ M}$

Sometimes it is possible to use chemical insight to find solutions to equilibrium problems without actually solving a quadratic (or more complicated) equation. First, however, it is useful to verify that equilibrium can be obtained starting from two extremes: all (or mostly) reactants and all (or mostly) products (similar to what was shown in [link](#)).

Consider the ionization of 0.150 M HA, a weak acid.

Equation:



The most obvious way to determine the equilibrium concentrations would be to start with only reactants. This could be called the “all reactant” starting point. Using x for the amount of acid ionized at equilibrium, this is the ICE table and solution.

	$\text{HA}(aq) \rightleftharpoons \text{H}^+(aq) + \text{A}^-(aq)$		
Initial concentration (M)	0.150	0	0
Change (M)	$-x$	x	x
Equilibrium concentration (M)	$0.150 - x$	x	x

Setting up and solving the quadratic equation gives

Equation:

$$K_c = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(x)(x)}{(0.150 - x)} = 6.80 \times 10^{-4}$$

Equation:

$$x^2 + 6.80 \times 10^{-4}x - 1.02 \times 10^{-4} = 0$$

Equation:

$$x = \frac{-6.80 \times 10^{-4} \pm \sqrt{(6.80 \times 10^{-4})^2 - (4)(1)(-1.02 \times 10^{-4})}}{(2)(1)}$$

Equation:

$$x = 0.00977 \text{ M or } -0.0104 \text{ M}$$

Using the positive (physical) root, the equilibrium concentrations are

Equation:

$$[\text{HA}] = 0.150 - x = 0.140 \text{ M}$$

Equation:

$$[\text{H}^+] = [\text{A}^-] = x = 0.00977 \text{ M}$$

A less obvious way to solve the problem would be to assume all the HA ionizes first, then the system comes to equilibrium. This could be called the “all product” starting point. Assuming all of the HA ionizes gives

Equation:

$$[\text{HA}] = 0.150 - 0.150 = 0 \text{ M}$$

Equation:

$$[\text{H}^+] = 0 + 0.150 = 0.150 \text{ M}$$

Equation:

$$[\text{A}^-] = 0 + 0.150 = 0.150 \text{ M}$$

Using these as initial concentrations and “y” to represent the concentration of HA at equilibrium, this is the ICE table for this starting point.

	$\text{HA(aq)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{A}^-(\text{aq})$		
Initial concentration (M)	0	0.150	0.150
Change (M)	+y	-y	-y
Equilibrium concentration (M)	y	0.150 - y	0.150 - y

Setting up and solving the quadratic equation gives

Equation:

$$K_c = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(0.150 - y)(0.150 - y)}{(y)} = 6.80 \times 10^{-4}$$

Equation:

$$6.80 \times 10^{-4}y = 0.0225 - 0.300y + y^2$$

Retain a few extra significant figures to minimize rounding problems.

Equation:

$$y^2 - 0.30068y + 0.022500 = 0$$

Equation:

$$y = \frac{0.30068 \pm \sqrt{(0.30068)^2 - (4)(1)(0.022500)}}{(2)(1)}$$

Equation:

$$y = \frac{0.30068 \pm 0.020210}{2}$$

Rounding each solution to three significant figures gives

Equation:

$$y = 0.160 \text{ M} \qquad \text{or} \qquad y = 0.140 \text{ M}$$

Using the physically significant root (0.140 M) gives the equilibrium concentrations as

Equation:

$$[\text{HA}] = y = 0.140 \text{ M}$$

Equation:

$$[\text{H}^+] = 0.150 - y = 0.010 \text{ M}$$

Equation:

$$[\text{A}^-] = 0.150 - y = 0.010 \text{ M}$$

Thus, the two approaches give the same results (to three *decimal places*), and show that *both* starting points lead to the same equilibrium conditions. The “all reactant” starting point resulted in a relatively small change (x) because the system was close to equilibrium, while the “all product” starting point had a relatively large change (y) that was nearly the size of the initial concentrations. It can be said that a system that starts “close” to equilibrium will require only a “small” change in conditions (x) to reach equilibrium.

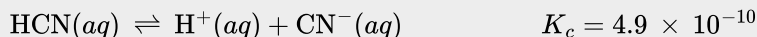
Recall that a small K_c means that very little of the reactants form products and a large K_c means that most of the reactants form products. If the system can be arranged so it starts “close” to equilibrium, then if the change (x) is small compared to any initial concentrations, it can be neglected. Small is usually defined as resulting in an error of less than 5%. The following two examples demonstrate this.

Example:

Approximate Solution Starting Close to Equilibrium

What are the concentrations at equilibrium of a 0.15 M solution of HCN?

Equation:



Solution

Using “ x ” to represent the concentration of each product at equilibrium gives this ICE table.

	$\text{HCN(aq)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{CN}^-(\text{aq})$		
Initial concentration (M)	0.15	0	0
Change (M)	$-x$	x	x
Equilibrium concentration (M)	$0.15 - x$	x	x

The exact solution may be obtained using the quadratic formula with

Equation:

$$K_c = \frac{(x)(x)}{0.15 - x}$$

solving

Equation:

$$x^2 + 4.9 \times 10^{-10} - 7.35 \times 10^{-11} = 0$$

Equation:

$$x = 8.56 \times 10^{-6} \text{ M (3 sig. figs.)} = 8.6 \times 10^{-6} \text{ M (2 sig. figs.)}$$

Thus $[\text{H}^+] = [\text{CN}^-] = x = 8.6 \times 10^{-6} \text{ M}$ and $[\text{HCN}] = 0.15 - x = 0.15 \text{ M}$.

In this case, chemical intuition can provide a simpler solution. From the equilibrium constant and the initial conditions, x must be small compared to 0.15 M . More formally, if $x \ll 0.15$, then $0.15 - x \approx 0.15$. If this assumption is true, then it simplifies obtaining x

Equation:

$$K_c = \frac{(x)(x)}{0.15 - x} \approx \frac{x^2}{0.15}$$

Equation:

$$4.9 \times 10^{-10} = \frac{x^2}{0.15}$$

Equation:

$$x^2 = (0.15)(4.9 \times 10^{-10}) = 7.4 \times 10^{-11}$$

Equation:

$$x = \sqrt{7.4 \times 10^{-11}} = 8.6 \times 10^{-6} \text{ M}$$

In this example, solving the exact (quadratic) equation and using approximations gave the same result to two significant figures. While most of the time the approximation is a bit different from the exact solution, as long as the error is less than 5%, the approximate solution is considered valid. In this problem, the 5% applies to IF ($0.15 - x \approx 0.15 \text{ M}$, so if

Equation:

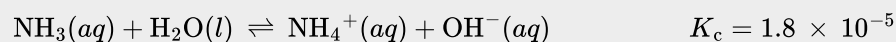
$$\frac{x}{0.15} \times 100\% = \frac{8.6 \times 10^{-6}}{0.15} \times 100\% = 0.006\%$$

is less than 5%, as it is in this case, the assumption is valid. The approximate solution is thus a valid solution.

Check Your Learning

What are the equilibrium concentrations in a 0.25 M NH₃ solution?

Equation:



Assume that x is much less than 0.25 M and calculate the error in your assumption.

Note:

Answer:

$[\text{OH}^-] = [\text{NH}_4^+] = 0.0021 \text{ M}$; $[\text{NH}_3] = 0.25 \text{ M}$, error = 0.84%

The second example requires that the original information be processed a bit, but it still can be solved using a small x approximation.

Example:

Approximate Solution After Shifting Starting Concentration

Copper(II) ions form a complex ion in the presence of ammonia

Equation:



If 0.010 mol Cu²⁺ is added to 1.00 L of a solution that is 1.00 M NH₃ what are the concentrations when the system comes to equilibrium?

Solution

The initial concentration of copper(II) is 0.010 M. The equilibrium constant is very large so it would be better to start with as much product as possible because “all products” is much closer to equilibrium than “all reactants.” Note that Cu²⁺ is the limiting reactant; if all 0.010 M of it reacts to form product the concentrations would be

Equation:

$$[\text{Cu}^{2+}] = 0.010 - 0.010 = 0 \text{ M}$$

Equation:

$$[\text{Cu}(\text{NH}_3)_4^{2+}] = 0.010 \text{ M}$$

Equation:

$$[\text{NH}_3] = 1.00 - 4 \times 0.010 = 0.96 \text{ M}$$

Using these “shifted” values as initial concentrations with x as the free copper(II) ion concentration at equilibrium gives this ICE table.

	$\text{Cu}^{2+}(\text{aq}) + 4\text{NH}_3(\text{aq}) \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}(\text{aq})$		
Initial concentration (M)	0	0.96	0.010
Change (M)	+x	+4x	-x
Equilibrium concentration (M)	x	0.96 + 4x	0.010 - x

Since we are starting close to equilibrium, x should be small so that

Equation:

$$0.96 + 4x \approx 0.96 \text{ M}$$

Equation:

$$0.010 - x \approx 0.010 \text{ M}$$

Equation:

$$K_c = \frac{(0.010 - x)}{x(0.96 - 4x)^4} \approx \frac{(0.010)}{x(0.96)^4} = 5.0 \times 10^{13}$$

Equation:

$$x = \frac{(0.010)}{K_c(0.96)^4} = 2.4 \times 10^{-16} \text{ M}$$

Select the smallest concentration for the 5% rule.

Equation:

$$\frac{2.4 \times 10^{-16}}{0.010} \times 100\% = 2 \times 10^{-12}\%$$

This is much less than 5%, so the assumptions are valid. The concentrations at equilibrium are

Equation:

$$[\text{Cu}^{2+}] = x = 2.4 \times 10^{-16} \text{ M}$$

Equation:

$$[\text{NH}_3] = 0.96 - 4x = 0.96 \text{ M}$$

Equation:

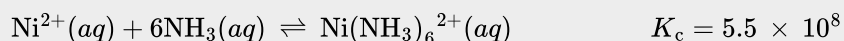
$$[\text{Cu}(\text{NH}_3)_4^{2+}] = 0.010 - x = 0.010 \text{ M}$$

By starting with the maximum amount of product, this system was near equilibrium and the change (x) was very small. With only a small change required to get to equilibrium, the equation for x was greatly simplified and gave a valid result well within the 5% error maximum.

Check Your Learning

What are the equilibrium concentrations when 0.25 mol Ni^{2+} is added to 1.00 L of 2.00 M NH_3 solution?

Equation:



With such a large equilibrium constant, first form as much product as possible, then assume that only a small amount (x) of the product shifts left. Calculate the error in your assumption.

Note:

Answer:

$$[\text{Ni}(\text{NH}_3)_6^{2+}] = 0.25 \text{ M}, [\text{NH}_3] = 0.50 \text{ M}, [\text{Ni}^{2+}] = 2.9 \times 10^{-8} \text{ M}, \text{error} = 1.2 \times 10^{-5}\%$$

Key Concepts and Summary

The ratios of the rate of change in concentrations of a reaction are equal to the ratios of the coefficients in the balanced chemical equation. The sign of the coefficient of x is positive when the concentration increases and negative when it decreases. We learned to approach three basic types of equilibrium problems. When given the concentrations of the reactants and products at equilibrium, we can solve for the equilibrium constant; when given the equilibrium constant and some of the concentrations involved, we can solve for the missing concentrations; and when given the equilibrium constant and the initial concentrations, we can solve for the concentrations at equilibrium.

Chemistry End of Chapter Exercises

Exercise:

Problem:

A reaction is represented by this equation: $\text{A}(aq) + 2\text{B}(aq) \rightleftharpoons 2\text{C}(aq)$ $K_c = 1 \times 10^3$

(a) Write the mathematical expression for the equilibrium constant.

(b) Using concentrations $\leq 1 \text{ M}$, make up two sets of concentrations that describe a mixture of A, B, and C at equilibrium.

Solution:

$$K_c = \frac{[\text{C}]^2}{[\text{A}][\text{B}]^2}. [\text{A}] = 0.1 \text{ M}, [\text{B}] = 0.1 \text{ M}, [\text{C}] = 1 \text{ M}; \text{ and } [\text{A}] = 0.01, [\text{B}] = 0.250, [\text{C}] = 0.791.$$

Exercise:

Problem:

A reaction is represented by this equation: $2\text{W}(aq) \rightleftharpoons \text{X}(aq) + 2\text{Y}(aq)$ $K_c = 5 \times 10^{-4}$

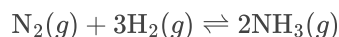
(a) Write the mathematical expression for the equilibrium constant.

(b) Using concentrations of $\leq 1 \text{ M}$, make up two sets of concentrations that describe a mixture of W, X, and Y at equilibrium.

Exercise:

Problem:

What is the value of the equilibrium constant at 500°C for the formation of NH_3 according to the following equation?



An equilibrium mixture of $\text{NH}_3(g)$, $\text{H}_2(g)$, and $\text{N}_2(g)$ at 500 °C was found to contain 1.35 M H_2 , 1.15 M N_2 , and 4.12×10^{-1} M NH_3 .

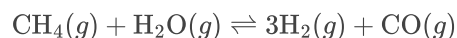
Solution:

$$K_c = 6.00 \times 10^{-2}$$

Exercise:

Problem:

Hydrogen is prepared commercially by the reaction of methane and water vapor at elevated temperatures.



What is the equilibrium constant for the reaction if a mixture at equilibrium contains gases with the following concentrations: CH_4 , 0.126 M; H_2O , 0.242 M; CO , 0.126 M; H_2 1.15 M, at a temperature of 760 °C?

Exercise:

Problem:

A 0.72-mol sample of PCl_5 is put into a 1.00-L vessel and heated. At equilibrium, the vessel contains 0.40 mol of $\text{PCl}_3(g)$ and 0.40 mol of $\text{Cl}_2(g)$. Calculate the value of the equilibrium constant for the decomposition of PCl_5 to PCl_3 and Cl_2 at this temperature.

Solution:

$$K_c = 0.50$$

Exercise:

Problem:

At 1 atm and 25 °C, NO_2 with an initial concentration of 1.00 M is $3.3 \times 10^{-3}\%$ decomposed into NO and O_2 . Calculate the value of the equilibrium constant for the reaction.



Exercise:

Problem:

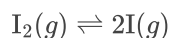
Calculate the value of the equilibrium constant K_P for the reaction $2\text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{NOCl}(g)$ from these equilibrium pressures: NO , 0.050 atm; Cl_2 , 0.30 atm; NOCl , 1.2 atm.

Solution:

$$K_P = 1.9 \times 10^3$$

Exercise:

Problem: When heated, iodine vapor dissociates according to this equation:



At 1274 K, a sample exhibits a partial pressure of I_2 of 0.1122 atm and a partial pressure due to I atoms of 0.1378 atm. Determine the value of the equilibrium constant, K_P , for the decomposition at 1274 K.

Exercise:

Problem: A sample of ammonium chloride was heated in a closed container.



At equilibrium, the pressure of $\text{NH}_3(g)$ was found to be 1.75 atm. What is the value of the equilibrium constant K_p for the decomposition at this temperature?

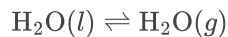
Solution:

$$K_p = 3.06$$

Exercise:

Problem:

At a temperature of 60 °C, the vapor pressure of water is 0.196 atm. What is the value of the equilibrium constant K_p for the transformation at 60 °C?

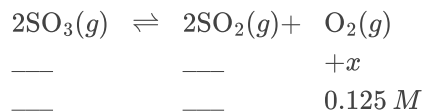


Exercise:

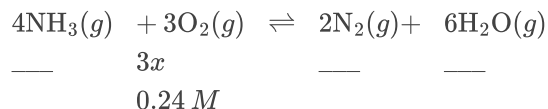
Problem:

Complete the changes in concentrations (or pressure, if requested) for each of the following reactions.

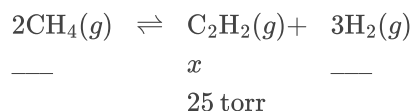
(a)



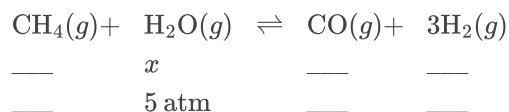
(b)



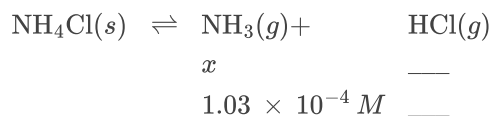
(c) Change in pressure:



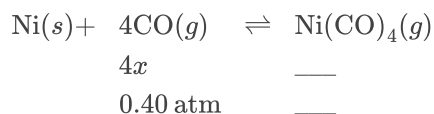
(d) Change in pressure:



(e)



(f) change in pressure:



Solution:

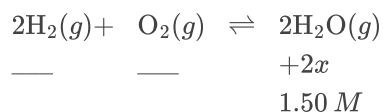
(a) $-2x$, $2x$, $-0.250 M$, $0.250 M$; (b) $4x$, $-2x$, $-6x$, $0.32 M$, $-0.16 M$, $-0.48 M$; (c) $-2x$, $3x$, -50 torr , 75 torr ; (d) x , $-x$, $-3x$, 5 atm , -5 atm , -15 atm ; (e) x , $1.03 \times 10^{-4} M$; (f) x , 0.1 atm .

Exercise:

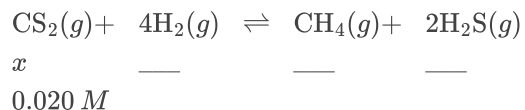
Problem:

Complete the changes in concentrations (or pressure, if requested) for each of the following reactions.

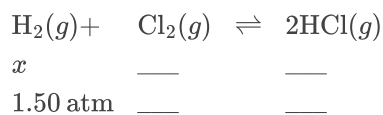
(a)



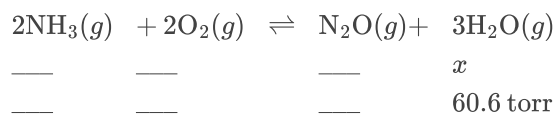
(b)



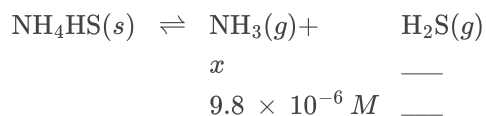
(c) Change in pressure:



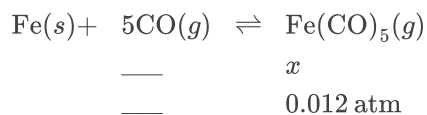
(d) Change in pressure:



(e)



(f) Change in pressure:



Exercise:

Problem: Why are there no changes specified for Ni in [\[link\]](#), part (f)? What property of Ni does change?

Solution:

Activities of pure crystalline solids equal 1 and are constant; however, the mass of Ni does change.

Exercise:

Problem:

Why are there no changes specified for NH₄HS in [\[link\]](#), part (e)? What property of NH₄HS does change?

Exercise:

Problem:

Analysis of the gases in a sealed reaction vessel containing NH₃, N₂, and H₂ at equilibrium at 400 °C established the concentration of N₂ to be 1.2 M and the concentration of H₂ to be 0.24 M.



Calculate the equilibrium molar concentration of NH₃.

Solution:

$$[\text{NH}_3] = 9.1 \times 10^{-2} \text{ M}$$

Exercise:

Problem:

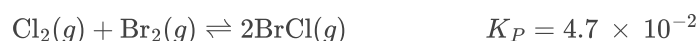
Calculate the number of moles of HI that are at equilibrium with 1.25 mol of H₂ and 1.25 mol of I₂ in a 5.00-L flask at 448 °C.



Exercise:

Problem:

What is the pressure of BrCl in an equilibrium mixture of Cl₂, Br₂, and BrCl if the pressure of Cl₂ in the mixture is 0.115 atm and the pressure of Br₂ in the mixture is 0.450 atm?



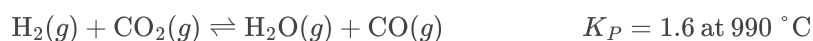
Solution:

$$P_{\text{BrCl}} = 4.9 \times 10^{-2} \text{ atm}$$

Exercise:

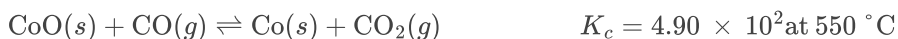
Problem:

What is the pressure of CO₂ in a mixture at equilibrium that contains 0.50 atm H₂, 2.0 atm of H₂O, and 1.0 atm of CO at 990 °C?



Exercise:

Problem: Cobalt metal can be prepared by reducing cobalt(II) oxide with carbon monoxide.



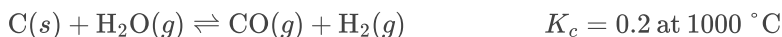
What concentration of CO remains in an equilibrium mixture with $[\text{CO}_2] = 0.100\text{ M}$?

Solution:

$$[\text{CO}] = 2.04 \times 10^{-4}\text{ M}$$

Exercise:

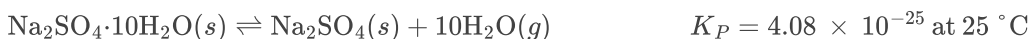
Problem: Carbon reacts with water vapor at elevated temperatures.



What is the concentration of CO in an equilibrium mixture with $[\text{H}_2\text{O}] = 0.500\text{ M}$ at 1000°C ?

Exercise:

Problem: Sodium sulfate 10-hydrate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, dehydrates according to the equation



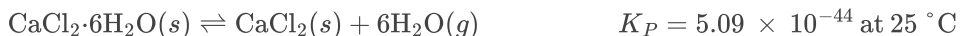
What is the pressure of water vapor at equilibrium with a mixture of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and Na_2SO_4 ?

Solution:

$$P_{\text{H}_2\text{O}} = 3.64 \times 10^{-3}\text{ atm}$$

Exercise:

Problem: Calcium chloride 6-hydrate, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, dehydrates according to the equation

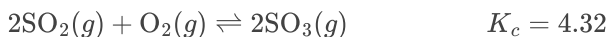


What is the pressure of water vapor at equilibrium with a mixture of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and CaCl_2 ?

Exercise:

Problem:

A student solved the following problem and found the equilibrium concentrations to be $[\text{SO}_2] = 0.590\text{ M}$, $[\text{O}_2] = 0.0450\text{ M}$, and $[\text{SO}_3] = 0.260\text{ M}$. How could this student check the work without reworking the problem? The problem was: For the following reaction at 600°C :



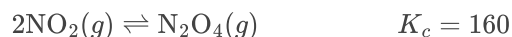
Solution:

Calculate Q based on the calculated concentrations and see if it is equal to K_c . Because Q does equal 4.32, the system must be at equilibrium.

Exercise:

Problem:

A student solved the following problem and found $[\text{N}_2\text{O}_4] = 0.16\text{ M}$ at equilibrium. How could this student recognize that the answer was wrong without reworking the problem? The problem was: What is the equilibrium concentration of N_2O_4 in a mixture formed from a sample of NO_2 with a concentration of 0.10 M ?



Exercise:

Problem:

Assume that the change in concentration of N_2O_4 is small enough to be neglected in the following problem.

(a) Calculate the equilibrium concentration of both species in 1.00 L of a solution prepared from 0.129 mol of N_2O_4 with chloroform as the solvent.



(b) Show that the change is small enough to be neglected.

Solution:

(a) $[\text{NO}_2] = 1.17 \times 10^{-3} M$

$[\text{N}_2\text{O}_4] = 0.128 M$

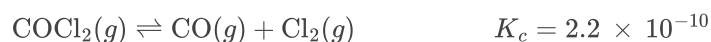
(b) Percent error = $\frac{5.87 \times 10^{-4}}{0.129} \times 100\% = 0.455\%$. The change in concentration of N_2O_4 is far less than the 5% maximum allowed.

Exercise:

Problem:

Assume that the change in concentration of COCl_2 is small enough to be neglected in the following problem.

(a) Calculate the equilibrium concentration of all species in an equilibrium mixture that results from the decomposition of COCl_2 with an initial concentration of 0.3166 M.



(b) Show that the change is small enough to be neglected.

Exercise:

Problem:

Assume that the change in pressure of H_2S is small enough to be neglected in the following problem.

(a) Calculate the equilibrium pressures of all species in an equilibrium mixture that results from the decomposition of H_2S with an initial pressure of 0.824 atm.



(b) Show that the change is small enough to be neglected.

Solution:

(a) $[\text{H}_2\text{S}] = 0.810 \text{ atm}$

$[\text{H}_2] = 0.014 \text{ atm}$

$[\text{S}_2] = 0.0072 \text{ atm}$

(b) The $2x$ is dropped from the equilibrium calculation because 0.014 is negligible when subtracted from 0.824. The percent error associated with ignoring $2x$ is $\frac{0.014}{0.824} \times 100\% = 1.7\%$, which is less than allowed by the "5% test." The error is, indeed, negligible.

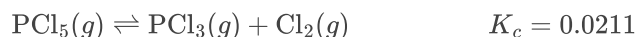
Exercise:

Problem:

What are all concentrations after a mixture that contains $[\text{H}_2\text{O}] = 1.00\text{ M}$ and $[\text{Cl}_2\text{O}] = 1.00\text{ M}$ comes to equilibrium at $25\text{ }^\circ\text{C}$?

**Exercise:****Problem:**

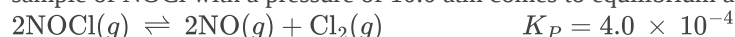
What are the concentrations of PCl_5 , PCl_3 , and Cl_2 in an equilibrium mixture produced by the decomposition of a sample of pure PCl_5 with $[\text{PCl}_5] = 2.00\text{ M}$?

**Solution:**

$[\text{PCl}_5] = 1.80\text{ M}$; $[\text{Cl}_2] = 0.195\text{ M}$; $[\text{PCl}_3] = 0.195\text{ M}$.

Exercise:**Problem:**

Calculate the pressures of all species at equilibrium in a mixture of NOCl , NO , and Cl_2 produced when a sample of NOCl with a pressure of 10.0 atm comes to equilibrium according to this reaction:

**Exercise:****Problem:**

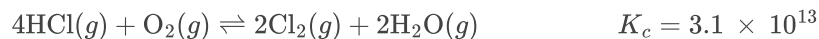
Calculate the equilibrium concentrations of NO , O_2 , and NO_2 in a mixture at $250\text{ }^\circ\text{C}$ that results from the reaction of 0.20 M NO and 0.10 M O_2 . (Hint: K is large; assume the reaction goes to completion then comes back to equilibrium.)

**Solution:**

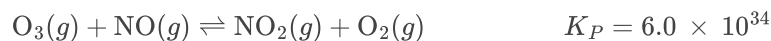
$[\text{NO}_2] = 0.19\text{ M}$
 $[\text{NO}] = 0.0070\text{ M}$
 $[\text{O}_2] = 0.0035\text{ M}$

Exercise:**Problem:**

Calculate the equilibrium concentrations that result when 0.25 M O_2 and 1.0 M HCl react and come to equilibrium.

**Exercise:**

Problem: One of the important reactions in the formation of smog is represented by the equation



What is the pressure of O_3 remaining after a mixture of O_3 with a pressure of $1.2 \times 10^{-8}\text{ atm}$ and NO with a pressure of $1.2 \times 10^{-8}\text{ atm}$ comes to equilibrium? (Hint: K_P is large; assume the reaction goes to completion)

then comes back to equilibrium.)

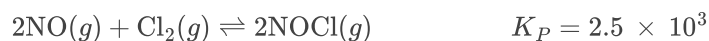
Solution:

$$P_{\text{O}_3} = 4.9 \times 10^{-26} \text{ atm}$$

Exercise:

Problem:

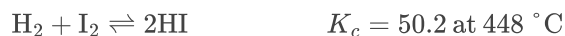
Calculate the pressures of NO, Cl₂, and NOCl in an equilibrium mixture produced by the reaction of a starting mixture with 4.0 atm NO and 2.0 atm Cl₂. (Hint: K_P is small; assume the reverse reaction goes to completion then comes back to equilibrium.)



Exercise:

Problem:

Calculate the number of grams of HI that are at equilibrium with 1.25 mol of H₂ and 63.5 g of iodine at 448 °C.

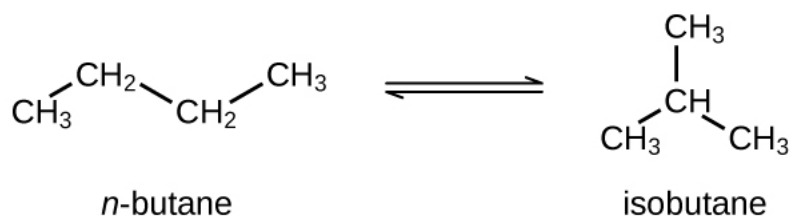


Solution:

507 g

Exercise:

Problem: Butane exists as two isomers, *n*-butane and isobutane.



$$K_P = 2.5 \text{ at } 25^\circ\text{C}$$

What is the pressure of isobutane in a container of the two isomers at equilibrium with a total pressure of 1.22 atm?

Exercise:

Problem:

What is the minimum mass of CaCO₃ required to establish equilibrium at a certain temperature in a 6.50-L container if the equilibrium constant (K_c) is 0.050 for the decomposition reaction of CaCO₃ at that temperature?

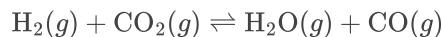


Solution:

33 g

Exercise:

Problem: The equilibrium constant (K_c) for this reaction is 1.60 at 990 °C:



Calculate the number of moles of each component in the final equilibrium mixture obtained from adding 1.00 mol of H_2 , 2.00 mol of CO_2 , 0.750 mol of H_2O , and 1.00 mol of CO to a 5.00-L container at 990 °C.

Exercise:

Problem:

At 25 °C and at 1 atm, the partial pressures in an equilibrium mixture of N_2O_4 and NO_2 are $P_{\text{N}_2\text{O}_4} = 0.70 \text{ atm}$ and $P_{\text{NO}_2} = 0.30 \text{ atm}$.

(a) Predict how the pressures of NO_2 and N_2O_4 will change if the total pressure increases to 9.0 atm. Will they increase, decrease, or remain the same?

(b) Calculate the partial pressures of NO_2 and N_2O_4 when they are at equilibrium at 9.0 atm and 25 °C.

Solution:

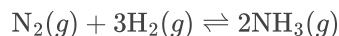
(a) Both gases must increase in pressure.

(b) $P_{\text{N}_2\text{O}_4} = 8.0 \text{ atm}$ and $P_{\text{NO}_2} = 1.0 \text{ atm}$

Exercise:

Problem:

In a 3.0-L vessel, the following equilibrium partial pressures are measured: N_2 , 190 torr; H_2 , 317 torr; NH_3 , $1.00 \times 10^3 \text{ torr}$.

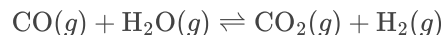


(a) How will the partial pressures of H_2 , N_2 , and NH_3 change if H_2 is removed from the system? Will they increase, decrease, or remain the same?

(b) Hydrogen is removed from the vessel until the partial pressure of nitrogen, at equilibrium, is 250 torr. Calculate the partial pressures of the other substances under the new conditions.

Exercise:

Problem: The equilibrium constant (K_c) for this reaction is 5.0 at a given temperature.



(a) On analysis, an equilibrium mixture of the substances present at the given temperature was found to contain 0.20 mol of CO , 0.30 mol of water vapor, and 0.90 mol of H_2 in a liter. How many moles of CO_2 were there in the equilibrium mixture?

(b) Maintaining the same temperature, additional H_2 was added to the system, and some water vapor was removed by drying. A new equilibrium mixture was thereby established containing 0.40 mol of CO , 0.30 mol of water vapor, and 1.2 mol of H_2 in a liter. How many moles of CO_2 were in the new equilibrium mixture? Compare this with the quantity in part (a), and discuss whether the second value is reasonable. Explain how it is possible for the water vapor concentration to be the same in the two equilibrium solutions even though some vapor was removed before the second equilibrium was established.

Solution:

(a) 0.33 mol.

(b) $[\text{CO}_2] = 0.50\text{ M}$ Added H_2 forms some water to compensate for the removal of water vapor and as a result of a shift to the left after H_2 is added.

Exercise:

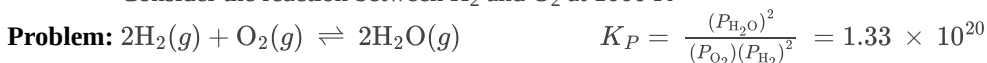
Problem: Antimony pentachloride decomposes according to this equation:



An equilibrium mixture in a 5.00-L flask at 448 °C contains 3.85 g of SbCl_5 , 9.14 g of SbCl_3 , and 2.84 g of Cl_2 . How many grams of each will be found if the mixture is transferred into a 2.00-L flask at the same temperature?

Exercise:

Consider the reaction between H_2 and O_2 at 1000 K



If 0.500 atm of H_2 and 0.500 atm of O_2 are allowed to come to equilibrium at this temperature, what are the partial pressures of the components?

Solution:

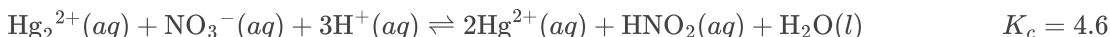
$$P_{\text{H}_2} = 8.64 \times 10^{-11} \text{ atm}$$

$$P_{\text{O}_2} = 0.250 \text{ atm}$$

$$P_{\text{H}_2\text{O}} = 0.500 \text{ atm}$$

Exercise:

Problem: An equilibrium is established according to the following equation



What will happen in a solution that is 0.20 M each in Hg_2^{2+} , NO_3^- , H^+ , Hg^{2+} , and HNO_2 ?

(a) Hg_2^{2+} will be oxidized and NO_3^- reduced.

(b) Hg_2^{2+} will be reduced and NO_3^- oxidized.

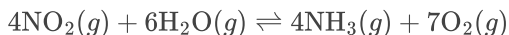
(c) Hg^{2+} will be oxidized and HNO_2 reduced.

(d) Hg^{2+} will be reduced and HNO_2 oxidized.

(e) There will be no change because all reactants and products have an activity of 1.

Exercise:

Problem: Consider the equilibrium



(a) What is the expression for the equilibrium constant (K_c) of the reaction?

(b) How must the concentration of NH_3 change to reach equilibrium if the reaction quotient is less than the equilibrium constant?

(c) If the reaction were at equilibrium, how would a decrease in pressure (from an increase in the volume of the reaction vessel) affect the pressure of NO_2 ?

(d) If the change in the pressure of NO_2 is 28 torr as a mixture of the four gases reaches equilibrium, how much will the pressure of O_2 change?

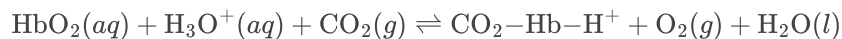
Solution:

(a) $K_c = \frac{[\text{NH}_3]^4[\text{O}_2]^7}{[\text{NO}_2]^4[\text{H}_2\text{O}]^6}$. (b) $[\text{NH}_3]$ must increase for Q_c to reach K_c . (c) That decrease in pressure would decrease $[\text{NO}_2]$. (d) $P_{\text{O}_2} = 49$ torr

Exercise:

Problem:

The binding of oxygen by hemoglobin (Hb), giving oxyhemoglobin (HbO_2), is partially regulated by the concentration of H_3O^+ and dissolved CO_2 in the blood. Although the equilibrium is complicated, it can be summarized as



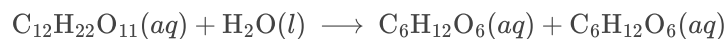
(a) Write the equilibrium constant expression for this reaction.

(b) Explain why the production of lactic acid and CO_2 in a muscle during exertion stimulates release of O_2 from the oxyhemoglobin in the blood passing through the muscle.

Exercise:

Problem:

The hydrolysis of the sugar sucrose to the sugars glucose and fructose follows a first-order rate equation for the disappearance of sucrose.



$$\text{Rate} = k[\text{C}_{12}\text{H}_{22}\text{O}_{11}]$$

In neutral solution, $k = 2.1 \times 10^{-11}/\text{s}$ at 27°C . (As indicated by the rate constant, this is a very slow reaction. In the human body, the rate of this reaction is sped up by a type of catalyst called an enzyme.) (Note: That is not a mistake in the equation—the products of the reaction, glucose and fructose, have the same molecular formulas, $\text{C}_6\text{H}_{12}\text{O}_6$, but differ in the arrangement of the atoms in their molecules). The equilibrium constant for the reaction is 1.36×10^5 at 27°C . What are the concentrations of glucose, fructose, and sucrose after a 0.150 M aqueous solution of sucrose has reached equilibrium? Remember that the activity of a solvent (the effective concentration) is 1.

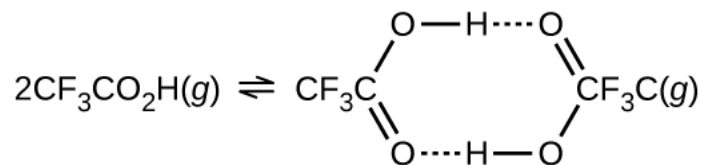
Solution:

$$[\text{fructose}] = 0.15\text{ M}$$

Exercise:

Problem:

The density of trifluoroacetic acid vapor was determined at 118.1°C and 468.5 torr, and found to be 2.784 g/L. Calculate K_c for the association of the acid.



Exercise:

Problem:

Liquid N_2O_3 is dark blue at low temperatures, but the color fades and becomes greenish at higher temperatures as the compound decomposes to NO and NO_2 . At 25°C , a value of $K_p = 1.91$ has been established for this decomposition. If 0.236 moles of N_2O_3 are placed in a 1.52-L vessel at 25°C , calculate the equilibrium partial pressures of $\text{N}_2\text{O}_3(g)$, $\text{NO}_2(g)$, and $\text{NO}(g)$.

Solution:

$$P_{\text{N}_2\text{O}_3} = 1.90 \text{ atm and } P_{\text{NO}} = P_{\text{NO}_2} = 1.90 \text{ atm}$$

Exercise:

Problem:

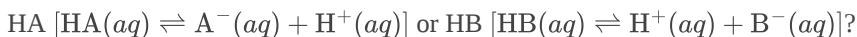
A 1.00-L vessel at 400°C contains the following equilibrium concentrations: N_2 , 1.00 M ; H_2 , 0.50 M ; and NH_3 , 0.25 M . How many moles of hydrogen must be removed from the vessel to increase the concentration of nitrogen to 1.1 M ?

Exercise:

Problem:

A 0.010 M solution of the weak acid HA has an osmotic pressure (see chapter on solutions and colloids) of 0.293 atm at 25°C . A 0.010 M solution of the weak acid HB has an osmotic pressure of 0.345 atm under the same conditions.

(a) Which acid has the larger equilibrium constant for ionization



(b) What are the equilibrium constants for the ionization of these acids?

(Hint: Remember that each solution contains three dissolved species: the weak acid (HA or HB), the conjugate base (A^- or B^-), and the hydrogen ion (H^+). Remember that osmotic pressure (like all colligative properties) is related to the total number of solute particles. Specifically for osmotic pressure, those concentrations are described by molarities.)

Solution:

(a) HB ionizes to a greater degree and has the larger K_c .

$$(b) K_c(\text{HA}) = 5 \times 10^{-4}$$

$$K_c(\text{HB}) = 3 \times 10^{-3}$$

Introduction

class="introduction"

- Brønsted-Lowry Acids and Bases
- pH and pOH
- Relative Strengths of Acids and Bases
- Hydrolysis of Salt Solutions
- Polyprotic Acids
- Buffers
- Acid-Base Titrations

Sinkholes
such as this
are the result
of reactions
between
acidic
groundwater
s and basic
rock
formations,
like
limestone.
(credit:
modification
of work by
Emil
Kehnel)



In our bodies, in our homes, and in our industrial society, acids and bases play key roles. Proteins, enzymes, blood, genetic material, and other components of living matter contain both acids and bases. We seem to like the sour taste of acids; we add them to soft drinks, salad dressings, and spices. Many foods, including citrus fruits and some vegetables, contain acids. Cleaners in our homes contain acids or bases. Acids and bases play important roles in the chemical industry. Currently, approximately 36 million metric tons of sulfuric acid are produced annually in the United States alone. Huge quantities of ammonia (8 million tons), urea (10 million tons), and phosphoric acid (10 million tons) are also produced annually.

This chapter will illustrate the chemistry of acid-base reactions and equilibria, and provide you with tools for quantifying the concentrations of acids and bases in solutions.

Quantitative Chemical Analysis

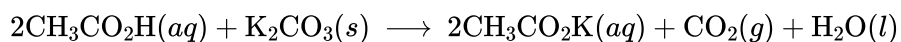
By the end of this section, you will be able to:

- Describe the fundamental aspects of titrations and gravimetric analysis.
- Perform stoichiometric calculations using typical titration and gravimetric data.

In the 18th century, the strength (actually the concentration) of vinegar samples was determined by noting the amount of potassium carbonate, K_2CO_3 , which had to be added, a little at a time, before bubbling ceased. The greater the weight of potassium carbonate added to reach the point where the bubbling ended, the more concentrated the vinegar.

We now know that the effervescence that occurred during this process was due to reaction with acetic acid, $\text{CH}_3\text{CO}_2\text{H}$, the compound primarily responsible for the odor and taste of vinegar. Acetic acid reacts with potassium carbonate according to the following equation:

Equation:

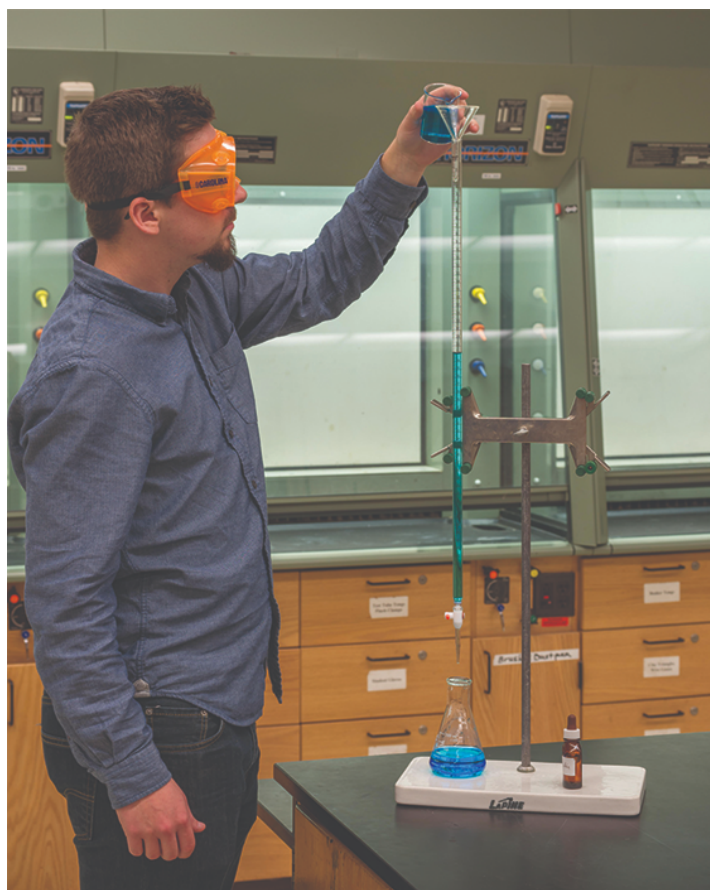


The bubbling was due to the production of CO_2 .

The test of vinegar with potassium carbonate is one type of **quantitative analysis**—the determination of the amount or concentration of a substance in a sample. In the analysis of vinegar, the concentration of the solute (acetic acid) was determined from the amount of reactant that combined with the solute present in a known volume of the solution. In other types of chemical analyses, the amount of a substance present in a sample is determined by measuring the amount of product that results.

Titration

The described approach to measuring vinegar strength was an early version of the analytical technique known as **titration analysis**. A typical titration analysis involves the use of a **buret** ([link](#)) to make incremental additions of a solution containing a known concentration of some substance (the **titrant**) to a sample solution containing the substance whose concentration is to be measured (the **analyte**). The titrant and analyte undergo a chemical reaction of known stoichiometry, and so measuring the volume of titrant solution required for complete reaction with the analyte (the **equivalence point** of the titration) allows calculation of the analyte concentration. The equivalence point of a titration may be detected visually if a distinct change in the appearance of the sample solution accompanies the completion of the reaction. The halt of bubble formation in the classic vinegar analysis is one such example, though, more commonly, special dyes called **indicators** are added to the sample solutions to impart a change in color at or very near the equivalence point of the titration. Equivalence points may also be detected by measuring some solution property that changes in a predictable way during the course of the titration. Regardless of the approach taken to detect a titration's equivalence point, the volume of titrant actually measured is called the **end point**. Properly designed titration methods typically ensure that the difference between the equivalence and end points is negligible. Though any type of chemical reaction may serve as the basis for a titration analysis, the three described in this chapter (precipitation, acid-base, and redox) are most common. Additional details regarding titration analysis are provided in the chapter on acid-base equilibria.



(a)



(b)

(a) A student fills a buret in preparation for a titration analysis. (b) A typical buret permits volume measurements to the nearest 0.01 mL. (credit a: modification of work by Mark Blaser and Matt Evans; credit b: modification of work by Mark Blaser and Matt Evans)

Example:
Titration Analysis

The end point in a titration of a 50.00-mL sample of aqueous HCl was reached by addition of 35.23 mL of 0.250 M NaOH titrant. The titration reaction is:

Equation:

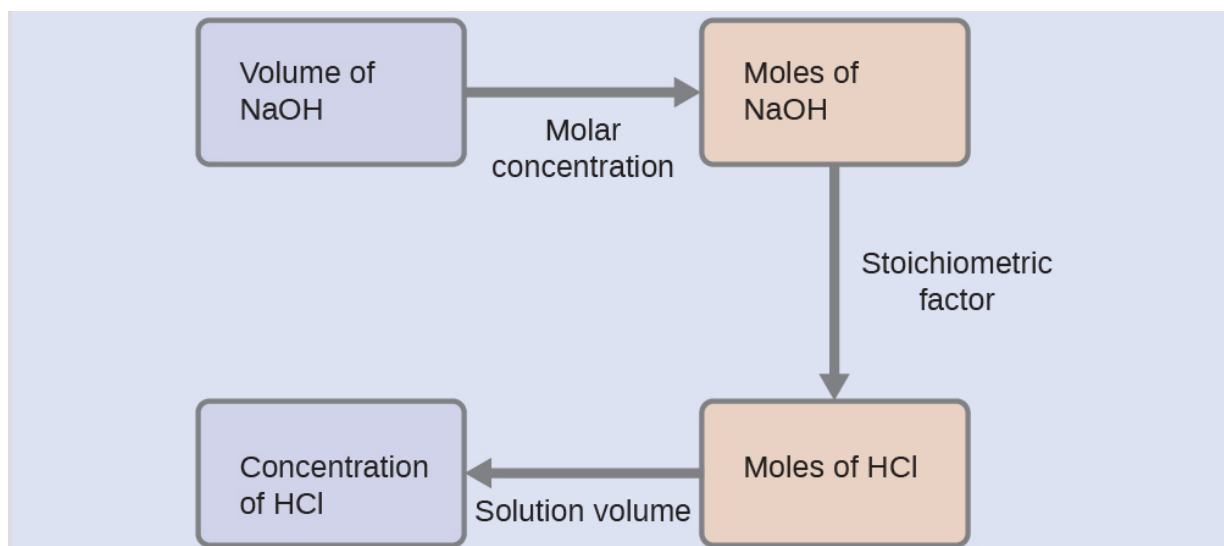


What is the molarity of the HCl?

Solution

As for all reaction stoichiometry calculations, the key issue is the relation between the molar amounts of the chemical species of interest as depicted in the balanced chemical equation. The approach outlined in previous modules of this chapter is followed, with additional considerations required, since the amounts of reactants provided and requested are expressed as solution concentrations.

For this exercise, the calculation will follow the following outlined steps:



The molar amount of HCl is calculated to be:

Equation:

$$35.23 \text{ mL NaOH} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.250 \text{ mol NaOH}}{1 \text{ L}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} = 8.81 \times 10^{-3} \text{ mol HCl}$$

Using the provided volume of HCl solution and the definition of molarity, the HCl concentration is:

Equation:

$$M = \frac{\text{mol HCl}}{\text{L solution}}$$

$$M = \frac{8.81 \times 10^{-3} \text{ mol HCl}}{50.00 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}}$$

$$M = 0.176 \text{ M}$$

Note: For these types of titration calculations, it is convenient to recognize that solution molarity is also equal to the number of *millimoles* of solute per *milliliter* of solution:

Equation:

$$M = \frac{\text{mol solute}}{\text{L solution}} \times \frac{\frac{10^3 \text{ mmol}}{\text{mol}}}{\frac{10^3 \text{ mL}}{\text{L}}} = \frac{\text{mmol solute}}{\text{mL solution}}$$

Using this version of the molarity unit will shorten the calculation by eliminating two conversion factors:

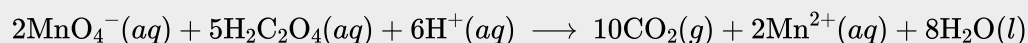
Equation:

$$\frac{35.23 \text{ mL NaOH} \times \frac{0.250 \text{ mmol NaOH}}{\text{mL NaOH}} \times \frac{1 \text{ mmol HCl}}{1 \text{ mmol NaOH}}}{50.00 \text{ mL solution}} = 0.176 \text{ M HCl}$$

Check Your Learning

A 20.00-mL sample of aqueous oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, was titrated with a 0.09113-M solution of potassium permanganate, KMnO_4 .

Equation:



A volume of 23.24 mL was required to reach the end point. What is the oxalic acid molarity?

Note:

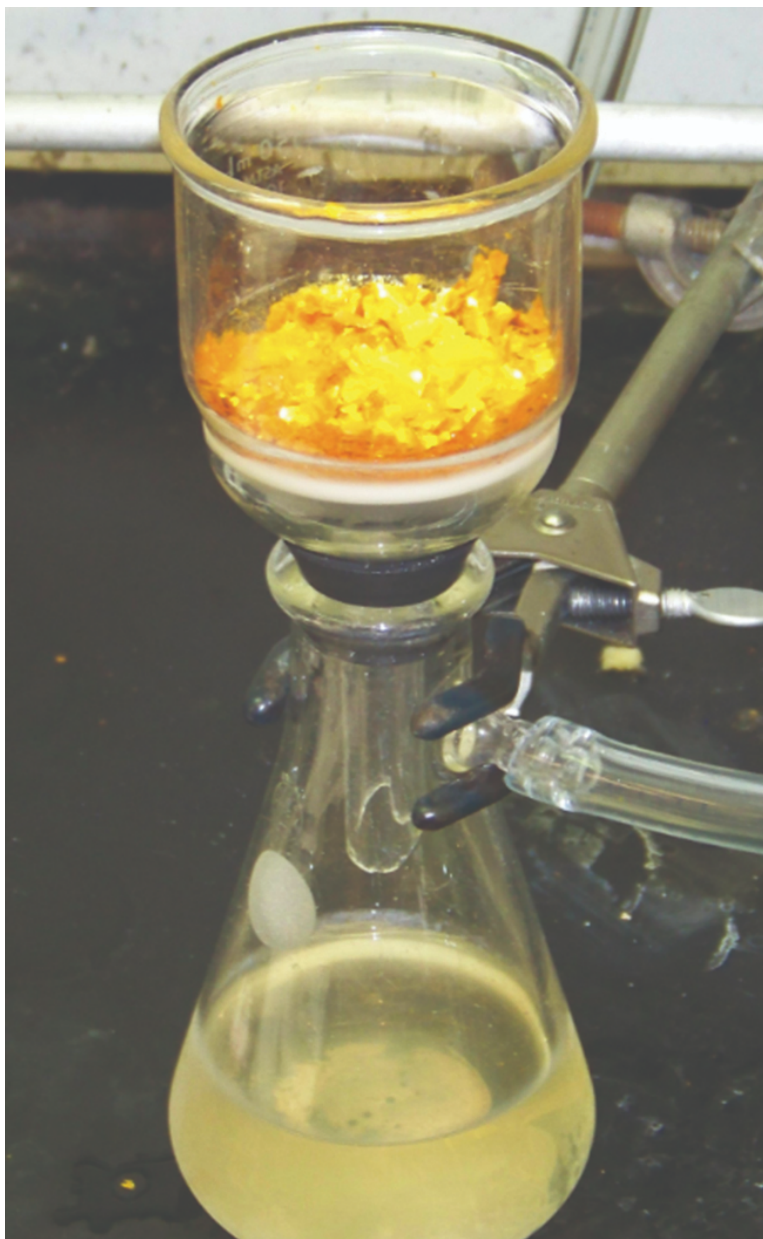
Answer:

0.2648 M

Gravimetric Analysis

A **gravimetric analysis** is one in which a sample is subjected to some treatment that causes a change in the physical state of the analyte that permits its separation from the other components of the sample. Mass measurements of the sample, the isolated analyte, or some other component of the analysis system, used along with the known stoichiometry of the compounds involved, permit calculation of the analyte concentration. Gravimetric methods were the first techniques used for quantitative chemical analysis, and they remain important tools in the modern chemistry laboratory.

The required change of state in a gravimetric analysis may be achieved by various physical and chemical processes. For example, the moisture (water) content of a sample is routinely determined by measuring the mass of a sample before and after it is subjected to a controlled heating process that evaporates the water. Also common are gravimetric techniques in which the analyte is subjected to a precipitation reaction of the sort described earlier in this chapter. The precipitate is typically isolated from the reaction mixture by filtration, carefully dried, and then weighed ([link](#)). The mass of the precipitate may then be used, along with relevant stoichiometric relationships, to calculate analyte concentration.



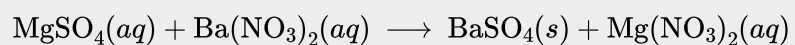
Precipitate may be removed from a reaction mixture by filtration.

Example:

Gravimetric Analysis

A 0.4550-g solid mixture containing MgSO_4 is dissolved in water and treated with an excess of $\text{Ba}(\text{NO}_3)_2$, resulting in the precipitation of 0.6168 g of BaSO_4 .

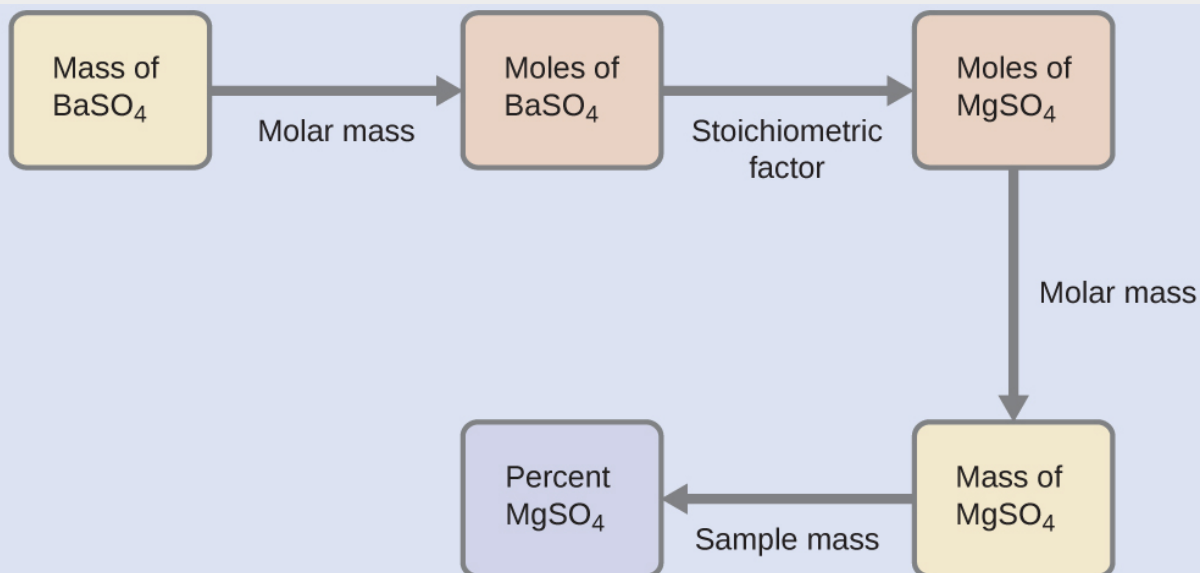
Equation:



What is the concentration (mass percent) of MgSO_4 in the mixture?

Solution

The plan for this calculation is similar to others used in stoichiometric calculations, the central step being the connection between the moles of BaSO_4 and MgSO_4 through their stoichiometric factor. Once the mass of MgSO_4 is computed, it may be used along with the mass of the sample mixture to calculate the requested percentage concentration.



The mass of MgSO_4 that would yield the provided precipitate mass is

Equation:

$$0.6168 \text{ g BaSO}_4 \times \frac{1 \text{ mol BaSO}_4}{233.43 \text{ g BaSO}_4} \times \frac{1 \text{ mol MgSO}_4}{1 \text{ mol BaSO}_4} \times \frac{120.37 \text{ g MgSO}_4}{1 \text{ mol MgSO}_4} = 0.3181 \text{ g MgSO}_4$$

The concentration of MgSO_4 in the sample mixture is then calculated to be

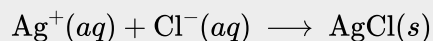
Equation:

$$\text{percent MgSO}_4 = \frac{\text{mass MgSO}_4}{\text{mass sample}} \times 100\%$$
$$\frac{0.3181 \text{ g}}{0.4550 \text{ g}} \times 100\% = 69.91\%$$

Check Your Learning

What is the percent of chloride ion in a sample if 1.1324 g of the sample produces 1.0881 g of AgCl when treated with excess Ag^+ ?

Equation:

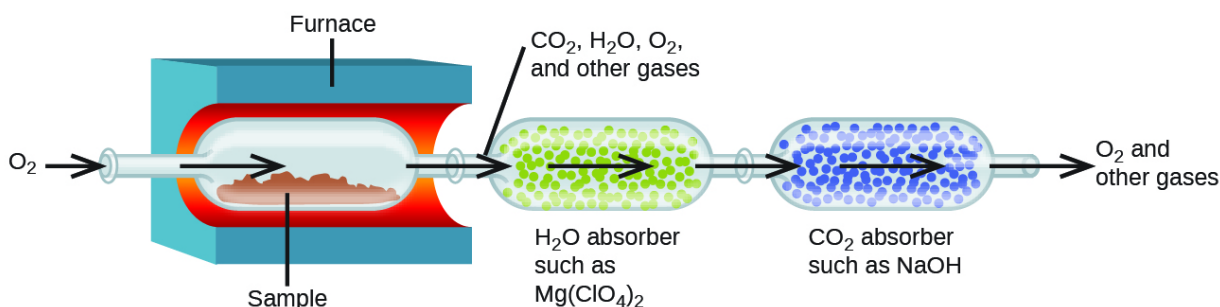


Note:

Answer:

23.76%

The elemental composition of hydrocarbons and related compounds may be determined via a gravimetric method known as **combustion analysis**. In a combustion analysis, a weighed sample of the compound is heated to a high temperature under a stream of oxygen gas, resulting in its complete combustion to yield gaseous products of known identities. The complete combustion of hydrocarbons, for example, will yield carbon dioxide and water as the only products. The gaseous combustion products are swept through separate, preweighed collection devices containing compounds that selectively absorb each product ([link](#)). The mass increase of each device corresponds to the mass of the absorbed product and may be used in an appropriate stoichiometric calculation to derive the mass of the relevant element.



This schematic diagram illustrates the basic components of a combustion analysis device for determining the carbon and hydrogen content of a sample.

Example:

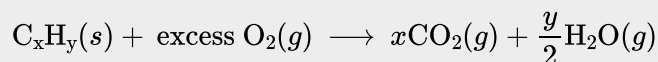
Combustion Analysis

Polyethylene is a hydrocarbon polymer used to produce food-storage bags and many other flexible plastic items. A combustion analysis of a 0.00126-g sample of polyethylene yields 0.00394 g of CO_2 and 0.00161 g of H_2O . What is the empirical formula of polyethylene?

Solution

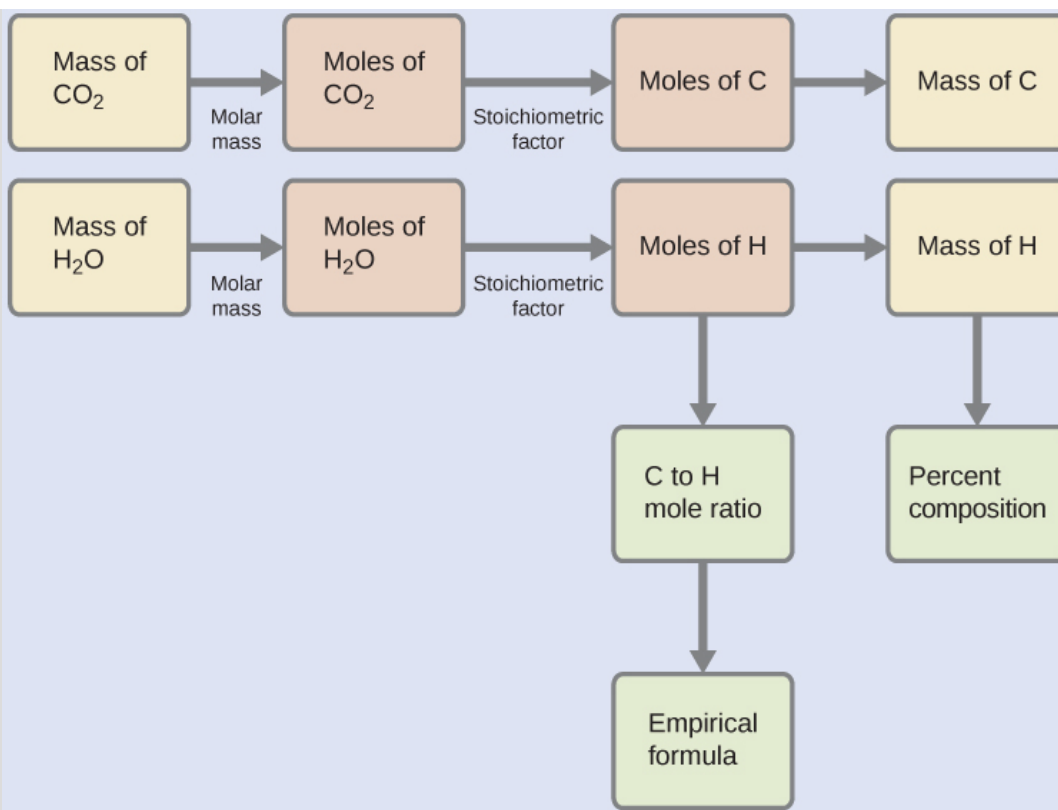
The primary assumption in this exercise is that all the carbon in the sample combusted is converted to carbon dioxide, and all the hydrogen in the sample is converted to water:

Equation:



Note that a balanced equation is not necessary for the task at hand. To derive the empirical formula of the compound, only the subscripts x and y are needed.

First, calculate the molar amounts of carbon and hydrogen in the sample, using the provided masses of the carbon dioxide and water, respectively. With these molar amounts, the empirical formula for the compound may be written as described in the previous chapter of this text. An outline of this approach is given in the following flow chart:



Equation:

$$\text{mol C} = 0.00394 \text{ g CO}_2 \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g}} \times \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} = 8.95 \times 10^{-5} \text{ mol C}$$

$$\text{mol H} = 0.00161 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g}} \times \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} = 1.79 \times 10^{-4} \text{ mol H}$$

The empirical formula for the compound is then derived by identifying the smallest whole-number multiples for these molar amounts. The H-to-C molar ratio is

Equation:

$$\frac{\text{mol H}}{\text{mol C}} = \frac{1.79 \times 10^{-4} \text{ mol H}}{8.95 \times 10^{-5} \text{ mol C}} = \frac{2 \text{ mol H}}{1 \text{ mol C}}$$

and the empirical formula for polyethylene is CH₂.

Check Your Learning

A 0.00215-g sample of polystyrene, a polymer composed of carbon and hydrogen, produced 0.00726 g of CO₂ and 0.00148 g of H₂O in a combustion analysis. What is the empirical formula for polystyrene?

Note:

Answer:

CH

Key Concepts and Summary

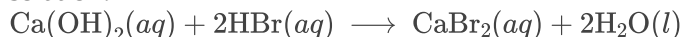
The stoichiometry of chemical reactions may serve as the basis for quantitative chemical analysis methods. Titrations involve measuring the volume of a titrant solution required to completely react with a sample solution. This volume is then used to calculate the concentration of analyte in the sample using the stoichiometry of the titration reaction. Gravimetric analysis involves separating the analyte from the sample by a physical or chemical process, determining its mass, and then calculating its concentration in the sample based on the stoichiometry of the relevant process. Combustion analysis is a gravimetric method used to determine the elemental composition of a compound by collecting and weighing the gaseous products of its combustion.

Chemistry End of Chapter Exercises

Exercise:

Problem:

What volume of 0.0105-M HBr solution is required to titrate 125 mL of a 0.0100-M $\text{Ca}(\text{OH})_2$ solution?



Exercise:

Problem:

Titration of a 20.0-mL sample of acid rain required 1.7 mL of 0.0811 M NaOH to reach the end point. If we assume that the acidity of the rain is due to the presence of sulfuric acid, what was the concentration of sulfuric acid in this sample of rain?

Solution:

$$3.4 \times 10^{-3} \text{ M H}_2\text{SO}_4$$

Exercise:

Problem:

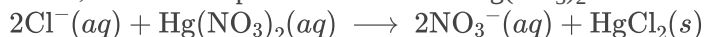
What is the concentration of NaCl in a solution if titration of 15.00 mL of the solution with 0.2503 M AgNO_3 requires 20.22 mL of the AgNO_3 solution to reach the end point?



Exercise:

Problem:

In a common medical laboratory determination of the concentration of free chloride ion in blood serum, a serum sample is titrated with a $\text{Hg}(\text{NO}_3)_2$ solution.



What is the Cl^- concentration in a 0.25-mL sample of normal serum that requires 1.46 mL of $8.25 \times 10^{-4} \text{ M Hg}(\text{NO}_3)_2(aq)$ to reach the end point?

Solution:

$$9.6 \times 10^{-3} \text{ M Cl}^-$$

Exercise:

Problem:

Potatoes can be peeled commercially by soaking them in a 3-M to 6-M solution of sodium hydroxide, then removing the loosened skins by spraying them with water. Does a sodium hydroxide solution have a suitable concentration if titration of 12.00 mL of the solution requires 30.6 mL of 1.65 M HCl to reach the end point?

Exercise:**Problem:**

A sample of gallium bromide, GaBr_3 , weighing 0.165 g was dissolved in water and treated with silver nitrate, AgNO_3 , resulting in the precipitation of 0.299 g AgBr . Use these data to compute the %Ga (by mass) GaBr_3 .

Solution:

22.4%

Exercise:**Problem:**

The principal component of mothballs is naphthalene, a compound with a molecular mass of about 130 amu, containing only carbon and hydrogen. A 3.000-mg sample of naphthalene burns to give 10.3 mg of CO_2 . Determine its empirical and molecular formulas.

Exercise:**Problem:**

A 0.025-g sample of a compound composed of boron and hydrogen, with a molecular mass of ~28 amu, burns spontaneously when exposed to air, producing 0.063 g of B_2O_3 . What are the empirical and molecular formulas of the compound?

Solution:

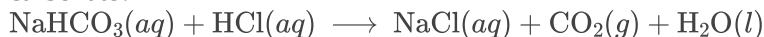
The empirical formula is BH_3 . The molecular formula is B_2H_6 .

Exercise:**Problem:**

Sodium bicarbonate (baking soda), NaHCO_3 , can be purified by dissolving it in hot water (60 °C), filtering to remove insoluble impurities, cooling to 0 °C to precipitate solid NaHCO_3 , and then filtering to remove the solid, leaving soluble impurities in solution. Any NaHCO_3 that remains in solution is not recovered. The solubility of NaHCO_3 in hot water of 60 °C is 164 g/L. Its solubility in cold water of 0 °C is 69 g/L. What is the percent yield of NaHCO_3 when it is purified by this method?

Exercise:**Problem:**

What volume of 0.600 M HCl is required to react completely with 2.50 g of sodium hydrogen carbonate?



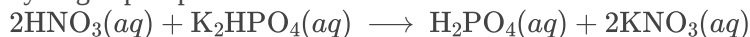
Solution:

49.6 mL

Exercise:

Problem:

What volume of 0.08892 *M* HNO₃ is required to react completely with 0.2352 g of potassium hydrogen phosphate?



Exercise:

Problem:

What volume of a 0.3300-*M* solution of sodium hydroxide would be required to titrate 15.00 mL of 0.1500 *M* oxalic acid?



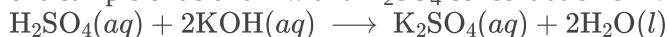
Solution:

13.64 mL

Exercise:

Problem:

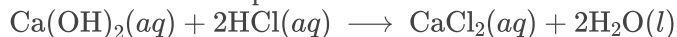
What volume of a 0.00945-*M* solution of potassium hydroxide would be required to titrate 50.00 mL of a sample of acid rain with a H₂SO₄ concentration of 1.23×10^{-4} *M*.



Exercise:

Problem:

A sample of solid calcium hydroxide, Ca(OH)₂, is allowed to stand in water until a saturated solution is formed. A titration of 75.00 mL of this solution with 5.00×10^{-2} *M* HCl requires 36.6 mL of the acid to reach the end point.



What is the molarity?

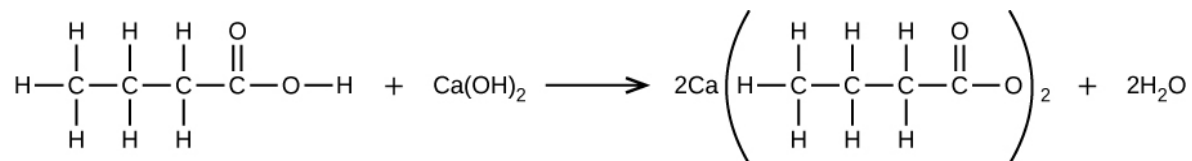
Solution:

0.0122 *M*

Exercise:

Problem:

What mass of Ca(OH)₂ will react with 25.0 g of butanoic to form the preservative calcium butanoate according to the equation?



Exercise:

Problem:

How many milliliters of a 0.1500-M solution of KOH will be required to titrate 40.00 mL of a 0.0656-M solution of H_3PO_4 ?

**Solution:**

34.99 mL KOH

Exercise:**Problem:**

Potassium acid phthalate, $\text{KNaC}_8\text{H}_4\text{O}_4$, or KHP, is used in many laboratories, including general chemistry laboratories, to standardize solutions of base. KHP is one of only a few stable solid acids that can be dried by warming and weighed. A 0.3420-g sample of $\text{KNaC}_8\text{H}_4\text{O}_4$ reacts with 35.73 mL of a NaOH solution in a titration. What is the molar concentration of the NaOH?

**Exercise:****Problem:**

The reaction of WCl_6 with Al at $\sim 400^\circ\text{C}$ gives black crystals of a compound containing only tungsten and chlorine. A sample of this compound, when reduced with hydrogen, gives 0.2232 g of tungsten metal and hydrogen chloride, which is absorbed in water. Titration of the hydrochloric acid thus produced requires 46.2 mL of 0.1051 M NaOH to reach the end point. What is the empirical formula of the black tungsten chloride?

Solution:

The empirical formula is WCl_4 .

Glossary

analyte

chemical species of interest

buret

device used for the precise delivery of variable liquid volumes, such as in a titration analysis

combustion analysis

gravimetric technique used to determine the elemental composition of a compound via the collection and weighing of its gaseous combustion products

end point

measured volume of titrant solution that yields the change in sample solution appearance or other property expected for stoichiometric equivalence (see *equivalence point*)

equivalence point

volume of titrant solution required to react completely with the analyte in a titration analysis; provides a stoichiometric amount of titrant for the sample's analyte according to the titration reaction

gravimetric analysis

quantitative chemical analysis method involving the separation of an analyte from a sample by a physical or chemical process and subsequent mass measurements of the analyte, reaction product, and/or sample

indicator

substance added to the sample in a titration analysis to permit visual detection of the end point

quantitative analysis

the determination of the amount or concentration of a substance in a sample

titrant

solution containing a known concentration of substance that will react with the analyte in a titration analysis

titration analysis

quantitative chemical analysis method that involves measuring the volume of a reactant solution required to completely react with the analyte in a sample

Brønsted-Lowry Acids and Bases

By the end of this section, you will be able to:

- Identify acids, bases, and conjugate acid-base pairs according to the Brønsted-Lowry definition
- Write equations for acid and base ionization reactions
- Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations
- Describe the acid-base behavior of amphoteric substances

Acids and bases have been known for a long time. When Robert Boyle characterized them in 1680, he noted that acids dissolve many substances, change the color of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact with alkalis (bases). In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO_2), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Svante Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

In an earlier chapter on chemical reactions, we defined acids and bases as Arrhenius did: We identified an acid as a compound that dissolves in water to yield hydronium ions (H_3O^+) and a base as a compound that dissolves in water to yield hydroxide ions (OH^-). This definition is not wrong; it is simply limited.

Later, we extended the definition of an acid or a base using the more general definition proposed in 1923 by the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry. Their definition centers on the proton, H^+ . A proton is what remains when the most common isotope of hydrogen, ^1_1H , loses an electron. A compound that donates a proton to another compound is called a **Brønsted-Lowry acid**, and a compound that accepts a proton is called a **Brønsted-Lowry base**. An acid-base reaction is the transfer of a proton from a proton donor (acid) to a proton acceptor (base). In a subsequent chapter of this text we will introduce the most general model of acid-base behavior introduced by the American chemist G. N. Lewis.

Acids may be compounds such as HCl or H_2SO_4 , organic acids like acetic acid (CH_3COOH) or ascorbic acid (vitamin C), or H_2O . Anions (such as HSO_4^- , H_2PO_4^- , HS^- , and HCO_3^-) and cations (such as H_3O^+ , NH_4^+ , and $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$) may also act as acids. Bases fall into the same three categories. Bases may be neutral molecules (such

as H_2O , NH_3 , and CH_3NH_2), anions (such as OH^- , HS^- , HCO_3^- , CO_3^{2-} , F^- , and PO_4^{3-}), or cations (such as $[\text{Al}(\text{H}_2\text{O})_5\text{OH}]^{2+}$). The most familiar bases are ionic compounds such as NaOH and $\text{Ca}(\text{OH})_2$, which contain the hydroxide ion, OH^- . The hydroxide ion in these compounds accepts a proton from acids to form water:

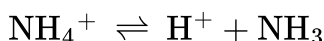
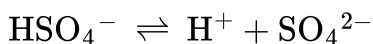
Equation:



We call the product that remains after an acid donates a proton the **conjugate base** of the acid. This species is a base because it can accept a proton (to re-form the acid):

Equation:

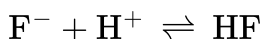
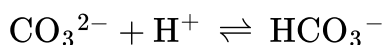
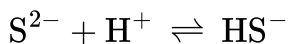
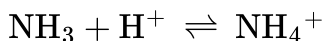
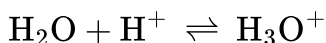
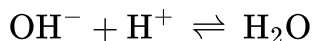
acid \rightleftharpoons proton + conjugate base



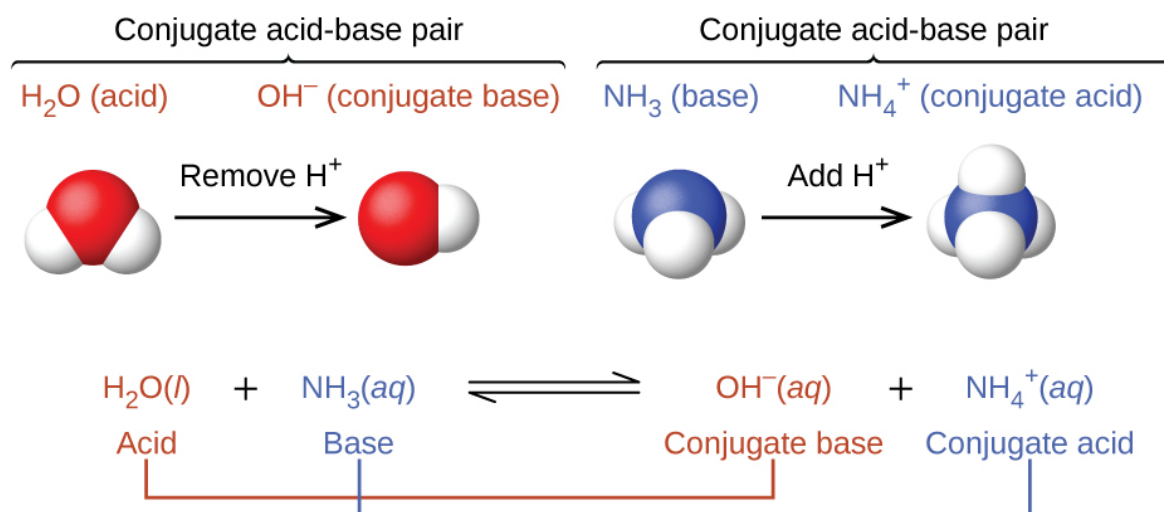
We call the product that results when a base accepts a proton the base's **conjugate acid**. This species is an acid because it can give up a proton (and thus re-form the base):

Equation:

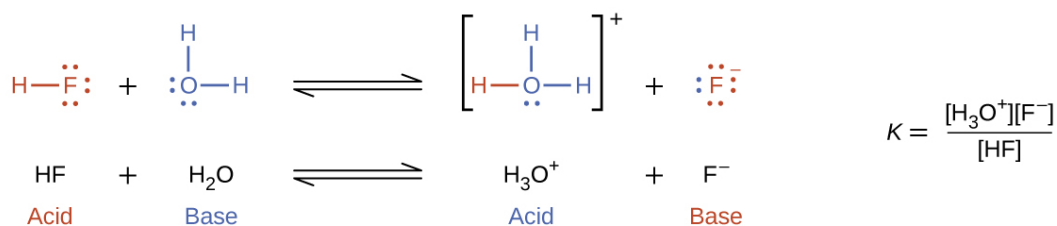
base + proton \rightleftharpoons conjugate acid



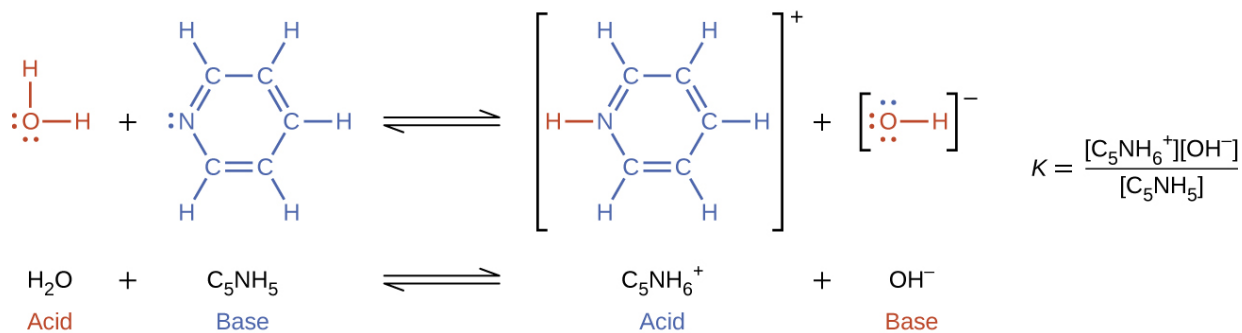
In these two sets of equations, the behaviors of acids as proton donors and bases as proton acceptors are represented in isolation. In reality, all acid-base reactions involve the *transfer* of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water, OH^- , and the conjugate acid of ammonia, NH_4^+ :



The reaction between a Brønsted-Lowry acid and water is called **acid ionization**. For example, when hydrogen fluoride dissolves in water and ionizes, protons are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:

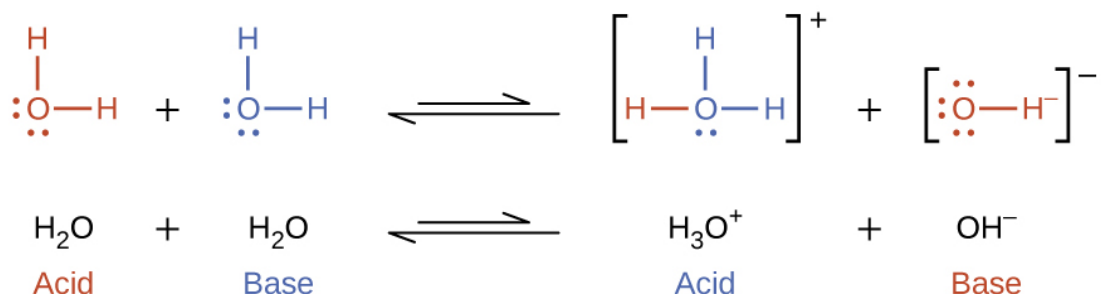


When we add a base to water, a **base ionization** reaction occurs in which protons are transferred from water molecules to base molecules. For example, adding pyridine to water yields hydroxide ions and pyridinium ions:



Notice that both these ionization reactions are represented as equilibrium processes. The relative extent to which these acid and base ionization reactions proceed is an important topic treated in a later section of this chapter. In the preceding paragraphs we saw that water can function as either an acid or a base, depending on the nature of the solute

dissolved in it. In fact, in pure water or in any aqueous solution, water acts both as an acid and a base. A very small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions:



This type of reaction, in which a substance ionizes when one molecule of the substance reacts with another molecule of the same substance, is referred to as **autoionization**.

Pure water undergoes autoionization to a very slight extent. Only about two out of every 10^9 molecules in a sample of pure water are ionized at 25 °C. The equilibrium constant for the ionization of water is called the **ion-product constant for water (K_w)**:

Equation:



The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, K_w has a value of 1.0×10^{-14} . The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for K_w is about 5.6×10^{-13} , roughly 50 times larger than the value at 25 °C.

Example:

Ion Concentrations in Pure Water

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

Solution

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water, $[\text{H}_3\text{O}^+] = [\text{OH}^-]$. At 25 °C:

Equation:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}_3\text{O}^+]^2 = [\text{OH}^-]^2 = 1.0 \times 10^{-14}$$

So:

Equation:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} \text{ M}$$

The hydronium ion concentration and the hydroxide ion concentration are the same, and we find that both equal $1.0 \times 10^{-7} \text{ M}$.

Check Your Learning

The ion product of water at 80°C is 2.4×10^{-13} . What are the concentrations of hydronium and hydroxide ions in pure water at 80°C ?

Note:

Answer:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 4.9 \times 10^{-7} \text{ M}$$

It is important to realize that the autoionization equilibrium for water is established in all aqueous solutions. Adding an acid or base to water will not change the position of the equilibrium. [\[link\]](#) demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations.

Example:

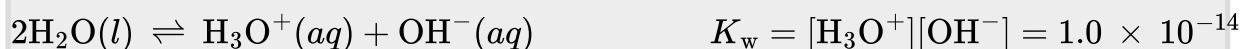
The Inverse Proportionality of $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$

A solution of carbon dioxide in water has a hydronium ion concentration of $2.0 \times 10^{-6} \text{ M}$. What is the concentration of hydroxide ion at 25°C ?

Solution

We know the value of the ion-product constant for water at 25°C :

Equation:



Thus, we can calculate the missing equilibrium concentration.

Rearrangement of the K_w expression yields that $[\text{OH}^-]$ is directly proportional to the inverse of $[\text{H}_3\text{O}^+]$:

Equation:

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9}$$

The hydroxide ion concentration in water is reduced to $5.0 \times 10^{-9} M$ as the hydronium ion concentration increases to $2.0 \times 10^{-6} M$. This is expected from Le Châtelier's principle; the autoionization reaction shifts to the left to reduce the stress of the increased hydronium ion concentration and the $[OH^-]$ is reduced relative to that in pure water.

A check of these concentrations confirms that our arithmetic is correct:

Equation:

$$K_w = [H_3O^+][OH^-] = (2.0 \times 10^{-6})(5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$

Check Your Learning

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of $0.001 M$ at $25^\circ C$?

Note:

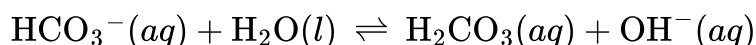
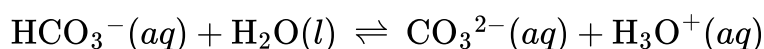
Answer:

$$[H_3O^+] = 1 \times 10^{-11} M$$

Amphiprotic Species

Like water, many molecules and ions may either gain or lose a proton under the appropriate conditions. Such species are said to be **amphiprotic**. Another term used to describe such species is **amphoteric**, which is a more general term for a species that may act either as an acid or a base by any definition (not just the Brønsted-Lowry one). Consider for example the bicarbonate ion, which may either donate or accept a proton as shown here:

Equation:



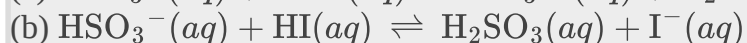
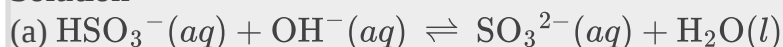
Example:

Representing the Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of HSO_3^-

(a) as an acid with OH^-

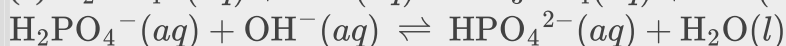
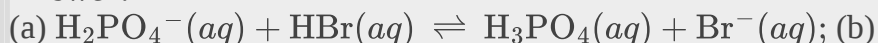
(b) as a base with HI

Solution**Check Your Learning**

Write separate equations representing the reaction of H_2PO_4^-

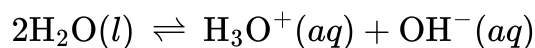
(a) as a base with HBr

(b) as an acid with OH^-

Note:**Answer:**

Key Concepts and Summary

A compound that can donate a proton (a hydrogen ion) to another compound is called a Brønsted-Lowry acid. The compound that accepts the proton is called a Brønsted-Lowry base. The species remaining after a Brønsted-Lowry acid has lost a proton is the conjugate base of the acid. The species formed when a Brønsted-Lowry base gains a proton is the conjugate acid of the base. Thus, an acid-base reaction occurs when a proton is transferred from an acid to a base, with formation of the conjugate base of the reactant acid and formation of the conjugate acid of the reactant base. Amphiprotic species can act as both proton donors and proton acceptors. Water is the most important amphiprotic species. It can form both the hydronium ion, H_3O^+ , and the hydroxide ion, OH^- when it undergoes autoionization:

Equation:

The ion product of water, K_w is the equilibrium constant for the autoionization reaction:

Equation:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

Key Equations

- $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ (at 25 °C)

Chemistry End of Chapter Exercises

Exercise:

Problem:

Write equations that show NH_3 as both a conjugate acid and a conjugate base.

Solution:

One example for NH_3 as a conjugate acid: $\text{NH}_2^- + \text{H}^+ \longrightarrow \text{NH}_3$; as a conjugate base: $\text{NH}_4^+(aq) + \text{OH}^-(aq) \longrightarrow \text{NH}_3(aq) + \text{H}_2\text{O}(l)$

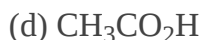
Exercise:

Problem: Write equations that show H_2PO_4^- acting both as an acid and as a base.

Exercise:

Problem:

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:



Solution:

(a) $\text{H}_3\text{O}^+(aq) \longrightarrow \text{H}^+(aq) + \text{H}_2\text{O}(l)$; (b) $\text{HCl}(aq) \longrightarrow \text{H}^+(aq) + \text{Cl}^-(aq)$; (c) $\text{NH}_3(aq) \longrightarrow \text{H}^+(aq) + \text{NH}_2^-(aq)$; (d) $\text{CH}_3\text{CO}_2\text{H}(aq) \longrightarrow \text{H}^+(aq) + \text{CH}_3\text{CO}_2^-(aq)$; (e) $\text{NH}_4^+(aq) \longrightarrow \text{H}^+(aq) + \text{NH}_3(aq)$; (f) $\text{HSO}_4^-(aq) \longrightarrow \text{H}^+(aq) + \text{SO}_4^{2-}(aq)$

Exercise:

Problem:

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

- (a) HNO_3
- (b) PH_4^+
- (c) H_2S
- (d) $\text{CH}_3\text{CH}_2\text{COOH}$
- (e) H_2PO_4^-
- (f) HS^-

Exercise:**Problem:**

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:

- (a) H_2O
- (b) OH^-
- (c) NH_3
- (d) CN^-
- (e) S^{2-}
- (f) H_2PO_4^-

Solution:

(a) $\text{H}_2\text{O}(l) + \text{H}^+(aq) \longrightarrow \text{H}_3\text{O}^+(aq)$; (b) $\text{OH}^-(aq) + \text{H}^+(aq) \longrightarrow \text{H}_2\text{O}(l)$; (c) $\text{NH}_3(aq) + \text{H}^+(aq) \longrightarrow \text{NH}_4^+(aq)$; (d) $\text{CN}^-(aq) + \text{H}^+(aq) \longrightarrow \text{HCN}(aq)$; (e) $\text{S}^{2-}(aq) + \text{H}^+(aq) \longrightarrow \text{HS}^-(aq)$; (f) $\text{H}_2\text{PO}_4^-(aq) + \text{H}^+(aq) \longrightarrow \text{H}_3\text{PO}_4(aq)$

Exercise:

Problem:

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:

- (a) HS^-
- (b) PO_4^{3-}
- (c) NH_2^-
- (d) $\text{C}_2\text{H}_5\text{OH}$
- (e) O^{2-}
- (f) H_2PO_4^-

Exercise:**Problem:**

What is the conjugate acid of each of the following? What is the conjugate base of each?

- (a) OH^-
- (b) H_2O
- (c) HCO_3^-
- (d) NH_3
- (e) HSO_4^-
- (f) H_2O_2
- (g) HS^-
- (h) H_5N_2^+

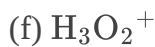
Solution:

(a) H_2O , O^{2-} ; (b) H_3O^+ , OH^- ; (c) H_2CO_3 , CO_3^{2-} ; (d) NH_4^+ , NH_2^- ; (e) H_2SO_4 , SO_4^{2-} ; (f) H_3O_2^+ , HO_2^- ; (g) H_2S , S^{2-} ; (h) $\text{H}_6\text{N}_2^{2+}$, H_4N_2

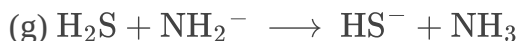
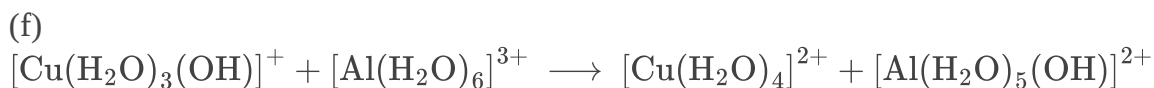
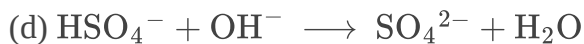
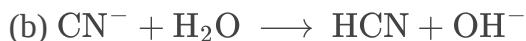
Exercise:

Problem:

What is the conjugate acid of each of the following? What is the conjugate base of each?

**Exercise:****Problem:**

Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:



Solution:

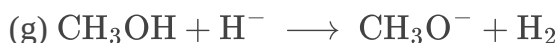
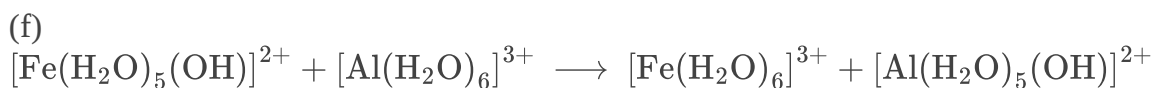
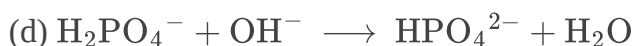
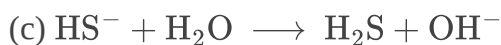
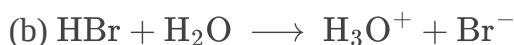
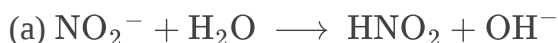
The labels are Brønsted-Lowry acid = BA; its conjugate base = CB; Brønsted-Lowry base = BB; its conjugate acid = CA. (a) HNO_3 (BA), H_2O (BB), H_3O^+ (CA),

NO₃⁻(CB); (b) CN⁻(BB), H₂O(BA), HCN(CA), OH⁻(CB); (c) H₂SO₄(BA), Cl⁻(BB), HCl(CA), HSO₄⁻(CB); (d) HSO₄⁻(BA), OH⁻(BB), SO₄²⁻(CB), H₂O(CA); (e) O²⁻(BB), H₂O(BA), OH⁻(CB and CA); (f) [Cu(H₂O)₃(OH)]⁺(BB), [Al(H₂O)₆]³⁺(BA), [Cu(H₂O)₄]²⁺(CA), [Al(H₂O)₅(OH)]²⁺(CB); (g) H₂S(BA), NH₂⁻(BB), HS⁻(CB), NH₃(CA)

Exercise:

Problem:

Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

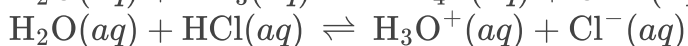


Exercise:

Problem: What are amphoteric species? Illustrate with suitable equations.

Solution:

Amphoteric species may either gain or lose a proton in a chemical reaction, thus acting as a base or an acid. An example is H₂O. As an acid:



Exercise:

Problem:

State which of the following species are amphoteric and write chemical equations illustrating the amphoteric character of these species:

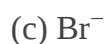




Exercise:

Problem:

State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species.



Solution:

amphiprotic: (a) $\text{NH}_3 + \text{H}_3\text{O}^+ \longrightarrow \text{NH}_4\text{OH} + \text{H}_2\text{O}$,
 $\text{NH}_3 + \text{OCH}_3^- \longrightarrow \text{NH}_2^- + \text{CH}_3\text{OH}$; (b)
 $\text{HPO}_4^{2-} + \text{OH}^- \longrightarrow \text{PO}_4^{3-} + \text{H}_2\text{O}$,
 $\text{HPO}_4^{2-} + \text{HClO}_4 \longrightarrow \text{H}_2\text{PO}_4^- + \text{ClO}_4^-$; not amphiprotic: (c) Br^- ; (d) NH_4^+ ;
(e) AsO_4^{3-}

Exercise:

Problem:

Is the self ionization of water endothermic or exothermic? The ionization constant for water (K_w) is 2.9×10^{-14} at 40 °C and 9.3×10^{-14} at 60 °C.

Glossary

acid ionization

reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

amphiprotic

species that may either gain or lose a proton in a reaction

amphoteric

species that can act as either an acid or a base

autoionization

reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

base ionization

reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

Brønsted-Lowry acid

proton donor

Brønsted-Lowry base

proton acceptor

conjugate acid

substance formed when a base gains a proton

conjugate base

substance formed when an acid loses a proton

ion-product constant for water (K_w)

equilibrium constant for the autoionization of water

pH and pOH

By the end of this section, you will be able to:

- Explain the characterization of aqueous solutions as acidic, basic, or neutral
- Express hydronium and hydroxide ion concentrations on the pH and pOH scales
- Perform calculations relating pH and pOH

As discussed earlier, hydronium and hydroxide ions are present both in pure water and in all aqueous solutions, and their concentrations are inversely proportional as determined by the ion product of water (K_w). The concentrations of these ions in a solution are often critical determinants of the solution's properties and the chemical behaviors of its other solutes, and specific vocabulary has been developed to describe these concentrations in relative terms. A solution is **neutral** if it contains equal concentrations of hydronium and hydroxide ions; **acidic** if it contains a greater concentration of hydronium ions than hydroxide ions; and **basic** if it contains a lesser concentration of hydronium ions than hydroxide ions.

A common means of expressing quantities, the values of which may span many orders of magnitude, is to use a logarithmic scale. One such scale that is very popular for chemical concentrations and equilibrium constants is based on the p-function, defined as shown where “X” is the quantity of interest and “log” is the base-10 logarithm:

Equation:

$$\text{pX} = -\log X$$

The **pH** of a solution is therefore defined as shown here, where $[\text{H}_3\text{O}^+]$ is the molar concentration of hydronium ion in the solution:

Equation:

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

Equation:

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or **pOH:**

Equation:

$$\text{pOH} = -\log[\text{OH}^-]$$

or

Equation:

$$[\text{OH}^-] = 10^{-\text{pOH}}$$

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the K_w expression:

Equation:

$$K_w = [\text{H}_3\text{O}^+] [\text{OH}^-]$$

Equation:

$$-\log K_w = -\log ([\text{H}_3\text{O}^+] [\text{OH}^-]) = -\log[\text{H}_3\text{O}^+] + -\log[\text{OH}^-]$$

Equation:

$$\text{p}K_w = \text{pH} + \text{pOH}$$

At 25 °C, the value of K_w is 1.0×10^{-14} , and so:

Equation:

$$14.00 = \text{pH} + \text{pOH}$$

As was shown in [\[link\]](#), the hydronium ion molarity in pure water (or any neutral solution) is $1.0 \times 10^{-7} M$ at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

Equation:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.0 \times 10^{-7}) = 7.00$$

Equation:

$$\text{pOH} = -\log[\text{OH}^-] = -\log(1.0 \times 10^{-7}) = 7.00$$

And so, *at this temperature*, acidic solutions are those with hydronium ion molarities greater than $1.0 \times 10^{-7} M$ and hydroxide ion molarities less than $1.0 \times 10^{-7} M$ (corresponding to pH values less than 7.00 and pOH values greater than 7.00). Basic solutions are those with hydronium ion molarities less than $1.0 \times 10^{-7} M$ and hydroxide ion molarities greater than $1.0 \times 10^{-7} M$ (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

Since the autoionization constant K_w is temperature dependent, these correlations between pH values and the acidic/neutral/basic adjectives will be different at temperatures other than 25 °C. For example, the “Check Your Learning” exercise accompanying [\[link\]](#) showed the hydronium molarity of pure water at 80 °C is $4.9 \times 10^{-7} M$, which corresponds to pH and pOH values of:

Equation:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(4.9 \times 10^{-7}) = 6.31$$

Equation:

$$\text{pOH} = -\log[\text{OH}^-] = -\log(4.9 \times 10^{-7}) = 6.31$$

At this temperature, then, neutral solutions exhibit $\text{pH} = \text{pOH} = 6.31$, acidic solutions exhibit pH less than 6.31 and pOH greater than 6.31, whereas

basic solutions exhibit pH greater than 6.31 and pOH less than 6.31. This distinction can be important when studying certain processes that occur at nonstandard temperatures, such as enzyme reactions in warm-blooded organisms. Unless otherwise noted, references to pH values are presumed to be those at standard temperature (25 °C) ([link](#)).

Summary of Relations for Acidic, Basic and Neutral Solutions		
Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[\text{H}_3\text{O}^+] > [\text{OH}^-]$	$\text{pH} < 7$
neutral	$[\text{H}_3\text{O}^+] = [\text{OH}^-]$	$\text{pH} = 7$
basic	$[\text{H}_3\text{O}^+] < [\text{OH}^-]$	$\text{pH} > 7$

[link](#) shows the relationships between $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$, pH, and pOH, and gives values for these properties at standard temperatures for some common substances.

$[\text{H}_3\text{O}^+]$ (M)	$[\text{OH}^-]$ (M)	pH	pOH	Sample Solution	
10^1	10^{-15}	-1	15		
10^0 or 1	10^{-14}	0	14	← 1 M HCl	acidic
10^{-1}	10^{-13}	1	13	← gastric juice	
10^{-2}	10^{-12}	2	12	← lime juice	
10^{-3}	10^{-11}	3	11	← 1 M $\text{CH}_3\text{CO}_2\text{H}$ (vinegar)	
10^{-4}	10^{-10}	4	10	← stomach acid	
10^{-5}	10^{-9}	5	9	← wine	
10^{-6}	10^{-8}	6	8	← orange juice	
10^{-7}	10^{-7}	7	7	← coffee	
10^{-8}	10^{-6}	8	6	← rain water	
10^{-9}	10^{-5}	9	5	← pure water	neutral
10^{-10}	10^{-4}	10	4	← blood	
10^{-11}	10^{-3}	11	3	← ocean water	
10^{-12}	10^{-2}	12	2	← baking soda	
10^{-13}	10^{-1}	13	1	← Milk of Magnesia	
10^{-14}	10^0 or 1	14	0	← household ammonia, NH_3	
10^{-15}	10^1	15	-1	← bleach	
				← 1 M NaOH	basic

The pH and pOH scales represent concentrations of $[\text{H}_3\text{O}^+]$ and OH^- , respectively. The pH and pOH values of some common substances at standard temperature (25 °C) are shown in this chart.

Example:

Calculation of pH from $[\text{H}_3\text{O}^+]$

What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of $1.2 \times 10^{-3} \text{ M}$?

Solution

Equation:

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

Equation:

$$= -\log(1.2 \times 10^{-3})$$

Equation:

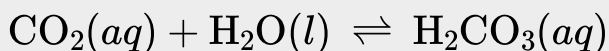
$$= -(-2.92) = 2.92$$

(The use of logarithms is explained in [Appendix B](#). Recall that, as we have done here, when taking the log of a value, keep as many decimal places in the result as there are significant figures in the value.)

Check Your Learning

Water exposed to air contains carbonic acid, H_2CO_3 , due to the reaction between carbon dioxide and water:

Equation:



Air-saturated water has a hydronium ion concentration caused by the dissolved CO_2 of $2.0 \times 10^{-6} M$, about 20-times larger than that of pure water. Calculate the pH of the solution at 25 °C.

Note:

Answer:

5.70

Example:

Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3 (slightly alkaline).

Solution

Equation:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 7.3$$

Equation:

$$\log[\text{H}_3\text{O}^+] = -7.3$$

Equation:

$$[\text{H}_3\text{O}^+] = 10^{-7.3} \text{ or } [\text{H}_3\text{O}^+] = \text{antilog of } -7.3$$

Equation:

$$[\text{H}_3\text{O}^+] = 5 \times 10^{-8} M$$

(On a calculator take the antilog, or the “inverse” log, of -7.3 , or calculate $10^{-7.3}$.)

Check Your Learning

Calculate the hydronium ion concentration of a solution with a pH of -1.07 .

Note:

Answer:

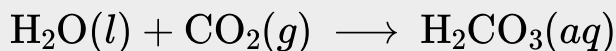
$12 M$

Note:

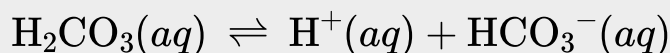
Environmental Science

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:

Equation:

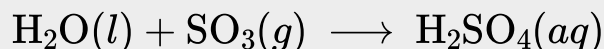


Equation:



Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO_2 , SO_2 , SO_3 , NO , and NO_2 being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

Equation:



Equation:



Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems from burning fossil fuels, which have traces of sulfur, and from the process of “roasting” ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes

uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone ([\[link\]](#)). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.

For further information on acid rain, visit this [website](#) hosted by the US Environmental Protection Agency.



(a)



(b)

(a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by “Eden, Janine and Jim”/Flickr)

Example:

Calculation of pOH

What are the pOH and the pH of a 0.0125-*M* solution of potassium hydroxide, KOH?

Solution

Potassium hydroxide is a highly soluble ionic compound and completely dissociates when dissolved in dilute solution, yielding $[\text{OH}^-] = 0.0125 \text{ M}$:

Equation:

$$\text{pOH} = -\log[\text{OH}^-] = -\log 0.0125$$

Equation:

$$= -(-1.903) = 1.903$$

The pH can be found from the pOH:

Equation:

$$\text{pH} + \text{pOH} = 14.00$$

Equation:

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.903 = 12.10$$

Check Your Learning

The hydronium ion concentration of vinegar is approximately $4 \times 10^{-3} \text{ M}$. What are the corresponding values of pOH and pH?

Note:

Answer:

$$\text{pOH} = 11.6, \text{pH} = 2.4$$

The acidity of a solution is typically assessed experimentally by measurement of its pH. The pOH of a solution is not usually measured, as it is easily calculated from an experimentally determined pH value. The pH of a solution can be directly measured using a pH meter ([\[link\]](#)).



(a)



(b)

(a) A research-grade pH meter used in a laboratory can have a resolution of 0.001 pH units, an accuracy of ± 0.002 pH units, and may cost in excess of \$1000. (b) A portable pH meter has lower resolution (0.01 pH units), lower accuracy (± 0.2 pH units), and a far lower price tag. (credit b: modification of work by Jacopo Werther)

The pH of a solution may also be visually estimated using colored indicators ([link](#)).



(a)



(b)

(a) A universal indicator assumes a different color in solutions of

different pH values. Thus, it can be added to a solution to determine the pH of the solution. The eight vials each contain a universal indicator and 0.1-*M* solutions of progressively weaker acids: HCl (pH = 1), CH₃CO₂H (pH = 3), and NH₄Cl (pH = 5), deionized water, a neutral substance (pH = 7); and 0.1-*M* solutions of the progressively stronger bases: KCl (pH = 7), aniline, C₆H₅NH₂ (pH = 9), NH₃ (pH = 11), and NaOH (pH = 13). (b) pH paper contains a mixture of indicators that give different colors in solutions of differing pH values.
(credit: modification of work by Sahar Atwa)

Key Concepts and Summary

The concentration of hydronium ion in a solution of an acid in water is greater than $1.0 \times 10^{-7} \text{ M}$ at 25 °C. The concentration of hydroxide ion in a solution of a base in water is greater than $1.0 \times 10^{-7} \text{ M}$ at 25 °C. The concentration of H₃O⁺ in a solution can be expressed as the pH of the solution; $\text{pH} = -\log[\text{H}_3\text{O}^+]$. The concentration of OH⁻ can be expressed as the pOH of the solution: $\text{pOH} = -\log[\text{OH}^-]$. In pure water, pH = 7.00 and pOH = 7.00

Key Equations

- $\text{pH} = -\log[\text{H}_3\text{O}^+]$
- $\text{pOH} = -\log[\text{OH}^-]$
- $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$
- $[\text{OH}^-] = 10^{-\text{pOH}}$
- $\text{pH} + \text{pOH} = \text{p}K_{\text{w}} = 14.00 \text{ at } 25 \text{ } ^\circ\text{C}$

Chemistry End of Chapter Exercises

Exercise:

Problem:

Explain why a sample of pure water at 40 °C is neutral even though $[\text{H}_3\text{O}^+] = 1.7 \times 10^{-7} \text{ M}$. K_w is 2.9×10^{-14} at 40 °C.

Solution:

In a neutral solution $[\text{H}_3\text{O}^+] = [\text{OH}^-]$. At 40 °C,
 $[\text{H}_3\text{O}^+] = [\text{OH}^-] = (2.9 \times 10^{-14})^{1/2} = 1.7 \times 10^{-7}$.

Exercise:**Problem:**

The ionization constant for water (K_w) is 2.9×10^{-14} at 40 °C.
Calculate $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$, pH, and pOH for pure water at 40 °C.

Exercise:**Problem:**

The ionization constant for water (K_w) is 9.311×10^{-14} at 60 °C.
Calculate $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$, pH, and pOH for pure water at 60 °C.

Solution:

$$\begin{aligned}x &= 3.051 \times 10^{-7} \text{ M} = [\text{H}_3\text{O}^+] = [\text{OH}^-] \\ \text{pH} &= -\log 3.051 \times 10^{-7} = -(-6.5156) = 6.5156 \\ \text{pOH} &= \text{pH} = 6.5156\end{aligned}$$

Exercise:**Problem:**

Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

(a) 0.200 M HCl

(b) 0.0143 M NaOH

(c) 3.0 M HNO_3

(d) 0.0031 M $\text{Ca}(\text{OH})_2$

Exercise:

Problem:

Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

(a) 0.000259 M HClO_4

(b) 0.21 M NaOH

(c) 0.000071 M $\text{Ba}(\text{OH})_2$

(d) 2.5 M KOH

Solution:

(a) pH = 3.587; pOH = 10.413; (b) pH = 0.68; pOH = 13.32; (c) pOH = 3.85; pH = 10.15; (d) pH = -0.40; pOH = 14.4

Exercise:

Problem:

What are the pH and pOH of a solution of 2.0 M HCl , which ionizes completely?

Exercise:

Problem:

What are the hydronium and hydroxide ion concentrations in a solution whose pH is 6.52?

Solution:

$[\text{H}_3\text{O}^+] = 3.0 \times 10^{-7} \text{ M}$; $[\text{OH}^-] = 3.3 \times 10^{-8} \text{ M}$

Exercise:**Problem:**

Calculate the hydrogen ion concentration and the hydroxide ion concentration in wine from its pH. See [\[link\]](#) for useful information.

Exercise:**Problem:**

Calculate the hydronium ion concentration and the hydroxide ion concentration in lime juice from its pH. See [\[link\]](#) for useful information.

Solution:

$$[\text{H}_3\text{O}^+] = 1 \times 10^{-2} \text{ M}; [\text{OH}^-] = 1 \times 10^{-12} \text{ M}$$

Exercise:**Problem:**

The hydronium ion concentration in a sample of rainwater is found to be $1.7 \times 10^{-6} \text{ M}$ at 25 °C. What is the concentration of hydroxide ions in the rainwater?

Exercise:**Problem:**

The hydroxide ion concentration in household ammonia is $3.2 \times 10^{-3} \text{ M}$ at 25 °C. What is the concentration of hydronium ions in the solution?

Solution:

$$[\text{OH}^-] = 3.1 \times 10^{-12} \text{ M}$$

Glossary

acidic

describes a solution in which $[\text{H}_3\text{O}^+] > [\text{OH}^-]$

basic

describes a solution in which $[\text{H}_3\text{O}^+] < [\text{OH}^-]$

neutral

describes a solution in which $[\text{H}_3\text{O}^+] = [\text{OH}^-]$

pH

logarithmic measure of the concentration of hydronium ions in a solution

pOH

logarithmic measure of the concentration of hydroxide ions in a solution

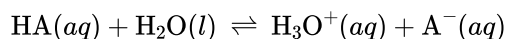
Relative Strengths of Acids and Bases

By the end of this section, you will be able to:

- Assess the relative strengths of acids and bases according to their ionization constants
- Rationalize trends in acid–base strength in relation to molecular structure
- Carry out equilibrium calculations for weak acid–base systems

We can rank the strengths of acids by the extent to which they ionize in aqueous solution. The reaction of an acid with water is given by the general expression:

Equation:



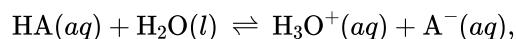
Water is the base that reacts with the acid HA, A^- is the conjugate base of the acid HA, and the hydronium ion is the conjugate acid of water. A strong acid yields 100% (or very nearly so) of H_3O^+ and A^- when the acid ionizes in water; [\[link\]](#) lists several strong acids. A weak acid gives small amounts of H_3O^+ and A^- .

6 Strong Acids		6 Strong Bases	
HClO_4	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$\text{Ca}(\text{OH})_2$	calcium hydroxide
HNO_3	nitric acid	$\text{Sr}(\text{OH})_2$	strontium hydroxide
H_2SO_4	sulfuric acid	$\text{Ba}(\text{OH})_2$	barium hydroxide

Some of the common strong acids and bases are listed here.

The relative strengths of acids may be determined by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions than do weaker acids. The equilibrium constant for an acid is called the **acid-ionization constant, K_a** . For the reaction of an acid HA:

Equation:



we write the equation for the ionization constant as:

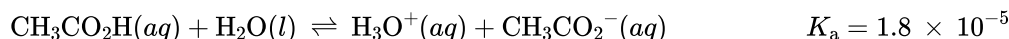
Equation:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

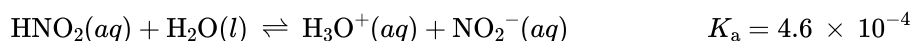
where the concentrations are those at equilibrium. Although water is a reactant in the reaction, it is the solvent as well, so we do not include $[H_2O]$ in the equation. The larger the K_a of an acid, the larger the concentration of H_3O^+ and A^- relative to the concentration of the nonionized acid, HA. Thus a stronger acid has a larger ionization constant than does a weaker acid. The ionization constants increase as the strengths of the acids increase. (A table of ionization constants of weak acids appears in [Appendix H](#), with a partial listing in [\[link\]](#).)

The following data on acid-ionization constants indicate the order of acid strength $CH_3CO_2H < HNO_2 < HSO_4^-$:

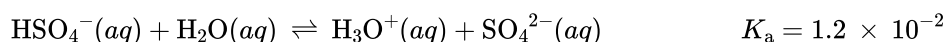
Equation:



Equation:



Equation:



Another measure of the strength of an acid is its percent ionization. The **percent ionization** of a weak acid is the ratio of the concentration of the ionized acid to the initial acid concentration, times 100:

Equation:

$$\% \text{ ionization} = \frac{[H_3O^+]_{eq}}{[HA]_0} \times 100$$

Because the ratio includes the initial concentration, the percent ionization for a solution of a given weak acid varies depending on the original concentration of the acid, and actually decreases with increasing acid concentration.

Example:

Calculation of Percent Ionization from pH

Calculate the percent ionization of a 0.125-M solution of nitrous acid (a weak acid), with a pH of 2.09.

Solution

The percent ionization for an acid is:

Equation:

$$\frac{[H_3O^+]_{eq}}{[HNO_2]_0} \times 100$$

The chemical equation for the dissociation of the nitrous acid is:

$HNO_2(aq) + H_2O(l) \rightleftharpoons NO_2^-(aq) + H_3O^+(aq)$. Since $10^{-pH} = [H_3O^+]$, we find that $10^{-2.09} = 8.1 \times 10^{-3} M$, so that percent ionization is:

Equation:

$$\frac{8.1 \times 10^{-3}}{0.125} \times 100 = 6.5 \%$$

Remember, the logarithm 2.09 indicates a hydronium ion concentration with only two significant figures.

Check Your Learning

Calculate the percent ionization of a 0.10-M solution of acetic acid with a pH of 2.89.

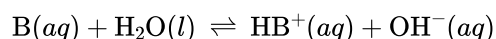
Note:

Answer:

1.3% ionized

We can rank the strengths of bases by their tendency to form hydroxide ions in aqueous solution. The reaction of a Brønsted-Lowry base with water is given by:

Equation:



Water is the acid that reacts with the base, HB^+ is the conjugate acid of the base B, and the hydroxide ion is the conjugate base of water. A strong base yields 100% (or very nearly so) of OH^- and HB^+ when it reacts with water; [\[link\]](#) lists several strong bases. A weak base yields a small proportion of hydroxide ions. Soluble ionic hydroxides such as NaOH are considered strong bases because they dissociate completely when dissolved in water.

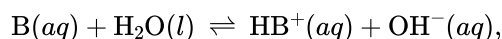
Note:



View the [simulation](#) of strong and weak acids and bases at the molecular level.

As we did with acids, we can measure the relative strengths of bases by measuring their **base-ionization constant** (K_b) in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, B:

Equation:



we write the equation for the ionization constant as:

Equation:

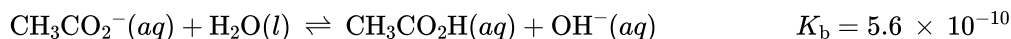
$$K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$$

where the concentrations are those at equilibrium. Again, we do not include $[\text{H}_2\text{O}]$ in the equation because water is the solvent. The chemical reactions and ionization constants of the three bases shown are:

Equation:



Equation:



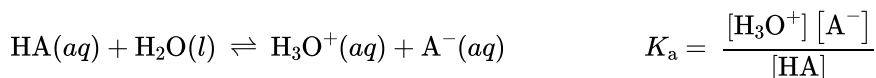
Equation:



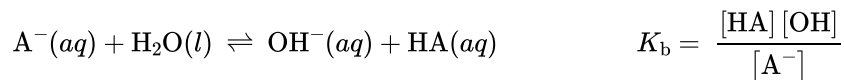
A table of ionization constants of weak bases appears in [Appendix I](#) (with a partial list in [\[link\]](#)). As with acids, percent ionization can be measured for basic solutions, but will vary depending on the base ionization constant and the initial concentration of the solution.

Consider the ionization reactions for a conjugate acid-base pair, $\text{HA} - \text{A}^-$:

Equation:

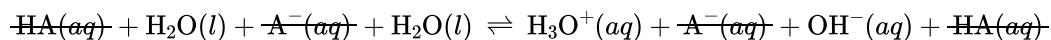


Equation:

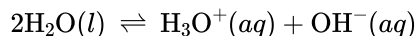


Adding these two chemical equations yields the equation for the autoionization for water:

Equation:



Equation:



Because of the way mass-action expressions are defined, the K expression for any chemical equation that is derived by adding together two or more other equations is equal to the mathematical product of the other equations' K expressions. Multiplying the mass-action expressions together and canceling common terms, we see that:

Equation:

$$K_a \times K_b = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \times \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w$$

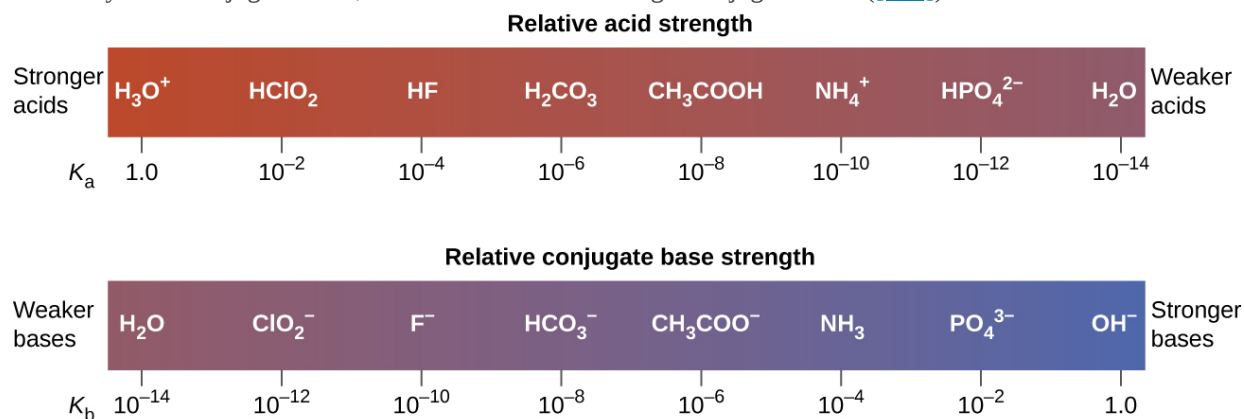
For example, the acid ionization constant of acetic acid (CH_3COOH) is 1.8×10^{-5} , and the base ionization constant of its conjugate base, acetate ion (CH_3COO^-), is 5.6×10^{-10} . The product of these two constants is indeed equal to K_w :

Equation:

$$K_a \times K_b = (1.8 \times 10^{-5}) \times (5.6 \times 10^{-10}) = 1.0 \times 10^{-14} = K_w$$


The extent to which an acid, HA , donates protons to water molecules depends on the strength of the conjugate base, A^- , of the acid. If A^- is a strong base, any protons that are donated to water molecules are recaptured by A^- . Thus there is relatively little A^- and H_3O^+ in solution, and the acid, HA , is weak. If A^- is a weak base, water

binds the protons more strongly, and the solution contains primarily A^- and H_3O^+ —the acid is strong. Strong acids form very weak conjugate bases, and weak acids form stronger conjugate bases ([link](#)).



This diagram shows the relative strengths of conjugate acid-base pairs, as indicated by their ionization constants in aqueous solution.

[link](#) lists a series of acids and bases in order of the decreasing strengths of the acids and the corresponding increasing strengths of the bases. The acid and base in a given row are conjugate to each other.

Acid			Base		
	perchloric acid	HClO_4	Do not undergo base ionization in water	ClO_4^-	perchlorate ion
	sulfuric acid	H_2SO_4		HSO_4^-	hydrogen sulfate ion
	hydrogen iodide	HI		I^-	iodide ion
	hydrogen bromide	HBr		Br^-	bromide ion
	hydrogen chloride	HCl		Cl^-	chloride ion
	nitric acid	HNO_3		NO_3^-	nitrate ion
	hydronium ion	H_3O^+		H_2O	water
	hydrogen sulfate ion	HSO_4^-		SO_4^{2-}	sulfate ion
	phosphoric acid	H_3PO_4		H_2PO_4^-	dihydrogen phosphate ion
	hydrogen fluoride	HF		F^-	fluoride ion
	nitrous acid	HNO_2		NO_2^-	nitrite ion
	acetic acid	$\text{CH}_3\text{CO}_2\text{H}$		CH_3CO_2^-	acetate ion
	carbonic acid	H_2CO_3		HCO_3^-	hydrogen carbonate ion
	hydrogen sulfide	H_2S		HS^-	hydrogen sulfide ion
	ammonium ion	NH_4^+		NH_3	ammonia
	hydrogen cyanide	HCN		CN^-	cyanide ion
	hydrogen carbonate ion	HCO_3^-		CO_3^{2-}	carbonate ion
	water	H_2O		OH^-	hydroxide ion
	hydrogen sulfide ion	HS^-	Undergo complete base ionization in water	S^{2-}	sulfide ion
	ethanol	$\text{C}_2\text{H}_5\text{OH}$		$\text{C}_2\text{H}_5\text{O}^-$	ethoxide ion
	ammonia	NH_3		NH_2^-	amide ion
	hydrogen	H_2		H^-	hydride ion
	methane	CH_4		CH_3^-	methide ion

The chart shows the relative strengths of conjugate acid-base pairs.

The first six acids in [\[link\]](#) are the most common strong acids. These acids are completely dissociated in aqueous solution. The conjugate bases of these acids are weaker bases than water. When one of these acids dissolves in water, their protons are completely transferred to water, the stronger base.

Those acids that lie between the hydronium ion and water in [\[link\]](#) form conjugate bases that can compete with water for possession of a proton. Both hydronium ions and nonionized acid molecules are present in equilibrium in a solution of one of these acids. Compounds that are weaker acids than water (those found below water in the column of acids) in [\[link\]](#) exhibit no observable acidic behavior when dissolved in water. Their conjugate bases are stronger than the hydroxide ion; if any conjugate base were formed, it would react with water to form the hydroxide ion.

The extent to which a base forms hydroxide ion in aqueous solution depends on the strength of the base relative to that of the hydroxide ion, as shown in the last column in [\[link\]](#). A strong base, such as one of those lying below hydroxide ion, accepts protons from water to yield 100% of the conjugate acid and hydroxide ion. Those bases lying between water and hydroxide ion accept protons from water, but a mixture of the hydroxide ion and the base

results. Bases that are weaker than water (those that lie above water in the column of bases) show no observable basic behavior in aqueous solution.

Example:

The Product $K_a \times K_b = K_w$

Use the K_b for the nitrite ion, NO_2^- , to calculate the K_a for its conjugate acid.

Solution

K_b for NO_2^- is given in this section as 2.17×10^{-11} . The conjugate acid of NO_2^- is HNO_2 ; K_a for HNO_2 can be calculated using the relationship:

Equation:

$$K_a \times K_b = 1.0 \times 10^{-14} = K_w$$

Solving for K_a , we get:

Equation:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{2.17 \times 10^{-11}} = 4.6 \times 10^{-4}$$

This answer can be verified by finding the K_a for HNO_2 in [Appendix H](#).

Check Your Learning

We can determine the relative acid strengths of NH_4^+ and HCN by comparing their ionization constants. The ionization constant of HCN is given in [Appendix H](#) as 4.9×10^{-10} . The ionization constant of NH_4^+ is not listed, but the ionization constant of its conjugate base, NH_3 , is listed as 1.8×10^{-5} . Determine the ionization constant of NH_4^+ , and decide which is the stronger acid, HCN or NH_4^+ .

Note:

Answer:

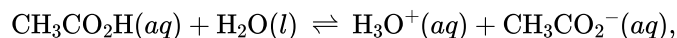
NH_4^+ is the slightly stronger acid (K_a for $\text{NH}_4^+ = 5.6 \times 10^{-10}$).

The Ionization of Weak Acids and Weak Bases

Many acids and bases are weak; that is, they do not ionize fully in aqueous solution. A solution of a weak acid in water is a mixture of the nonionized acid, hydronium ion, and the conjugate base of the acid, with the nonionized acid present in the greatest concentration. Thus, a weak acid increases the hydronium ion concentration in an aqueous solution (but not as much as the same amount of a strong acid).

Acetic acid, $\text{CH}_3\text{CO}_2\text{H}$, is a weak acid. When we add acetic acid to water, it ionizes to a small extent according to the equation:

Equation:



giving an equilibrium mixture with most of the acid present in the nonionized (molecular) form. This equilibrium, like other equilibria, is dynamic; acetic acid molecules donate hydrogen ions to water molecules and form hydronium ions and acetate ions at the same rate that hydronium ions donate hydrogen ions to acetate ions to reform acetic acid molecules and water molecules. We can tell by measuring the pH of an aqueous solution of

known concentration that only a fraction of the weak acid is ionized at any moment ([link](#)). The remaining weak acid is present in the nonionized form.

For acetic acid, at equilibrium:

Equation:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = 1.8 \times 10^{-5}$$



pH paper indicates that a 0.1-*M* solution of HCl (beaker on left) has a pH of 1. The acid is fully ionized and $[\text{H}_3\text{O}^+] = 0.1 \text{ M}$. A 0.1-*M* solution of $\text{CH}_3\text{CO}_2\text{H}$ (beaker on right) is a pH of 3 ($[\text{H}_3\text{O}^+] = 0.001 \text{ M}$) because the weak acid $\text{CH}_3\text{CO}_2\text{H}$ is only partially ionized. In this solution, $[\text{H}_3\text{O}^+] < [\text{CH}_3\text{CO}_2\text{H}]$. (credit: modification of work by Sahar Atwa)

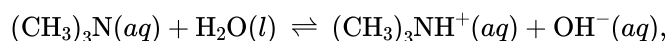
Ionization Constants of Some Weak Acids	
Ionization Reaction	K_a at 25 °C
$\text{HSO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{SO}_4^{2-}$	1.2×10^{-2}
$\text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^-$	3.5×10^{-4}
$\text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_2^-$	4.6×10^{-4}
$\text{HCNO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NCO}^-$	2×10^{-4}
$\text{HCO}_2\text{H} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HCO}_2^-$	1.8×10^{-4}
$\text{CH}_3\text{CO}_2\text{H} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{CO}_2^-$	1.8×10^{-5}
$\text{HClO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{ClO}^-$	2.9×10^{-8}
$\text{HBrO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{BrO}^-$	2.8×10^{-9}
$\text{HCN} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CN}^-$	4.9×10^{-10}

[\[link\]](#) gives the ionization constants for several weak acids; additional ionization constants can be found in [Appendix H](#).

At equilibrium, a solution of a weak base in water is a mixture of the nonionized base, the conjugate acid of the weak base, and hydroxide ion with the nonionized base present in the greatest concentration. Thus, a weak base increases the hydroxide ion concentration in an aqueous solution (but not as much as the same amount of a strong base).

For example, a solution of the weak base trimethylamine, $(\text{CH}_3)_3\text{N}$, in water reacts according to the equation:

Equation:



giving an equilibrium mixture with most of the base present as the nonionized amine. This equilibrium is analogous to that described for weak acids.

We can confirm by measuring the pH of an aqueous solution of a weak base of known concentration that only a fraction of the base reacts with water ([\[link\]](#)). The remaining weak base is present as the unreacted form. The equilibrium constant for the ionization of a weak base, K_b , is called the ionization constant of the weak base, and is equal to the reaction quotient when the reaction is at equilibrium. For trimethylamine, at equilibrium:

Equation:

$$K_b = \frac{[(\text{CH}_3)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3)_3\text{N}]}$$



pH paper indicates that a 0.1-*M* solution of NH_3 (left) is weakly basic. The solution has a pOH of 3 ($[\text{OH}^-] = 0.001 \text{ M}$) because the weak base NH_3 only partially reacts with water. A 0.1-*M* solution of NaOH (right) has a pOH of 1 because NaOH is a strong base. (credit: modification of work by Sahar Atwa)

The ionization constants of several weak bases are given in [\[link\]](#) and in [Appendix I](#).

Ionization Constants of Some Weak Bases	
Ionization Reaction	K_b at 25 °C
$(\text{CH}_3)_2\text{NH} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_2\text{NH}_2^+ + \text{OH}^-$	5.9×10^{-4}
$\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_3^+ + \text{OH}^-$	4.4×10^{-4}
$(\text{CH}_3)_3\text{N} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_3\text{NH}^+ + \text{OH}^-$	6.3×10^{-5}
$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	1.8×10^{-5}
$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	4.3×10^{-10}

Example:

Determination of K_a from Equilibrium Concentrations

Acetic acid is the principal ingredient in vinegar ([\[link\]](#)); that's why it tastes sour. At equilibrium, a solution contains $[\text{CH}_3\text{CO}_2\text{H}] = 0.0787 \text{ M}$ and $[\text{H}_3\text{O}^+] = [\text{CH}_3\text{CO}_2^-] = 0.00118 \text{ M}$. What is the value of K_a for acetic acid?

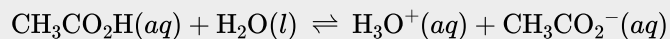


Vinegar is a solution of acetic acid, a weak acid. (credit: modification of work by “HomeSpot HQ”/Flickr)

Solution

We are asked to calculate an equilibrium constant from equilibrium concentrations. At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

Equation:



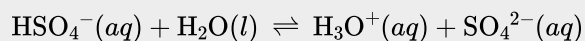
Equation:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = \frac{(0.00118)(0.00118)}{0.0787} = 1.77 \times 10^{-5}$$

Check Your Learning

What is the equilibrium constant for the ionization of the HSO_4^- ion, the weak acid used in some household cleansers:

Equation:



In one mixture of NaHSO_4 and Na_2SO_4 at equilibrium, $[\text{H}_3\text{O}^+] = 0.027 \text{ M}$; $[\text{HSO}_4^-] = 0.29 \text{ M}$; and $[\text{SO}_4^{2-}] = 0.13 \text{ M}$.

Note:

Answer:

$$K_a \text{ for } \text{HSO}_4^- = 1.2 \times 10^{-2}$$

Example:

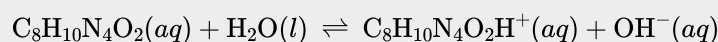
Determination of K_b from Equilibrium Concentrations

Caffeine, $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$ is a weak base. What is the value of K_b for caffeine if a solution at equilibrium has $[\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2] = 0.050 \text{ M}$, $[\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2\text{H}^+] = 5.0 \times 10^{-3} \text{ M}$, and $[\text{OH}^-] = 2.5 \times 10^{-3} \text{ M}$?

Solution

At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

Equation:



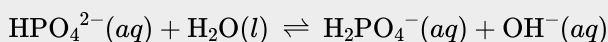
Equation:

$$K_b = \frac{[\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2\text{H}^+][\text{OH}^-]}{[\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2]} = \frac{(5.0 \times 10^{-3})(2.5 \times 10^{-3})}{0.050} = 2.5 \times 10^{-4}$$

Check Your Learning

What is the equilibrium constant for the ionization of the HPO_4^{2-} ion, a weak base:

Equation:



In a solution containing a mixture of NaH_2PO_4 and Na_2HPO_4 at equilibrium, $[\text{OH}^-] = 1.3 \times 10^{-6} \text{ M}$; $[\text{H}_2\text{PO}_4^-] = 0.042 \text{ M}$; and $[\text{HPO}_4^{2-}] = 0.341 \text{ M}$.

Note:

Answer:

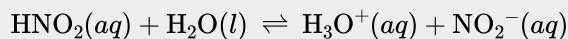
$$K_b \text{ for } \text{HPO}_4^{2-} = 1.6 \times 10^{-7}$$

Example:

Determination of K_a or K_b from pH

The pH of a 0.0516-M solution of nitrous acid, HNO_2 , is 2.34. What is its K_a ?

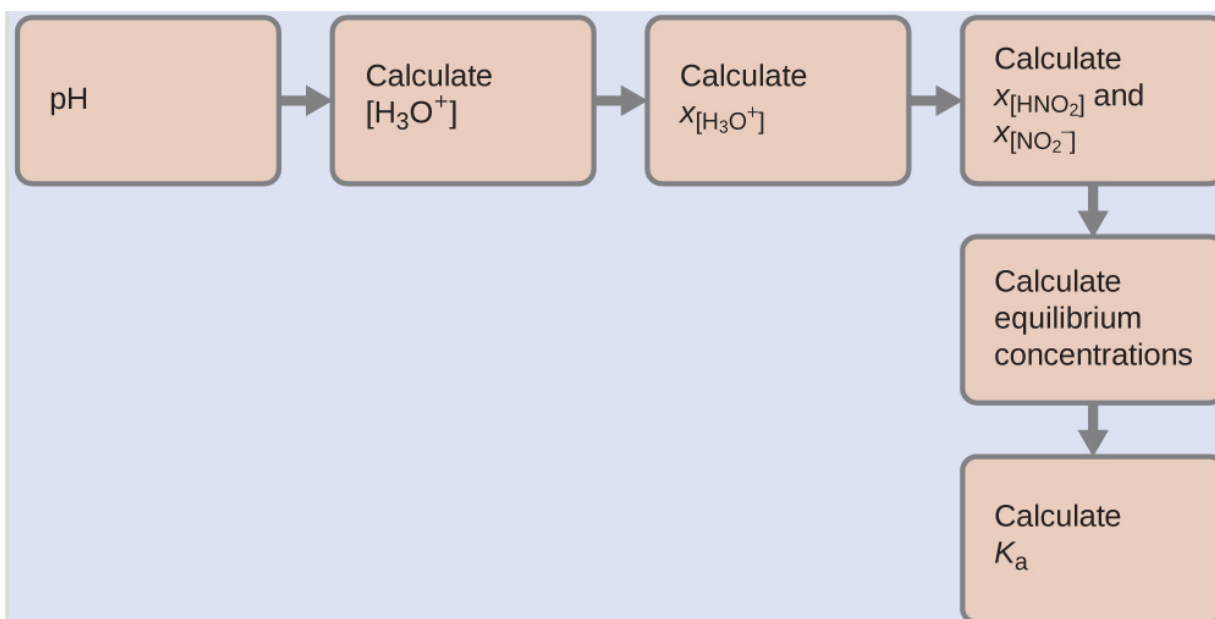
Equation:



Solution

We determine an equilibrium constant starting with the initial concentrations of HNO_2 , H_3O^+ , and NO_2^- as well as one of the final concentrations, the concentration of hydronium ion at equilibrium. (Remember that pH is simply another way to express the concentration of hydronium ion.)

We can solve this problem with the following steps in which x is a change in concentration of a species in the reaction:



To get the various values in the ICE (Initial, Change, Equilibrium) table, we first calculate $[\text{H}_3\text{O}^+]$, the equilibrium concentration of H_3O^+ , from the pH:

Equation:

$$[\text{H}_3\text{O}^+] = 10^{-2.34} = 0.0046 \text{ M}$$

The change in concentration of H_3O^+ , $x_{[\text{H}_3\text{O}^+]}$, is the difference between the equilibrium concentration of H_3O^+ , which we determined from the pH, and the initial concentration, $[\text{H}_3\text{O}^+]_i$. The initial concentration of H_3O^+ is its concentration in pure water, which is so much less than the final concentration that we approximate it as zero (~ 0).

The change in concentration of NO_2^- is equal to the change in concentration of $[\text{H}_3\text{O}^+]$. For each 1 mol of H_3O^+ that forms, 1 mol of NO_2^- forms. The equilibrium concentration of HNO_2 is equal to its initial concentration plus the change in its concentration.

Now we can fill in the ICE table with the concentrations at equilibrium, as shown here:

	$\text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_2^-$			
Initial concentration (M)	0.0516		~ 0	0
Change (M)	$-x$	+	$x = 0.0046$	$x = 0.0046$
Equilibrium concentration (M)	0.0470		0.0046	0.0046

Finally, we calculate the value of the equilibrium constant using the data in the table:

Equation:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = \frac{(0.0046)(0.0046)}{(0.0470)} = 4.5 \times 10^{-4}$$

Check Your Learning.

The pH of a solution of household ammonia, a 0.950-M solution of NH_3 , is 11.612. What is K_b for NH_3 .

Note:

Answer:

$$K_b = 1.8 \times 10^{-5}$$

Example:

Equilibrium Concentrations in a Solution of a Weak Acid

Formic acid, HCO_2H , is the irritant that causes the body's reaction to ant stings ([link](#)).



The pain of an ant's sting is caused by formic acid. (credit: John Tann)

What is the concentration of hydronium ion and the pH in a 0.534-M solution of formic acid?

Equation:



Solution

Determine x . The **Equation:**
and equilibrium
equilibrium expression $\text{HCO}_2\text{H}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HCO}_2^-(aq)$
concentrations:

The The table
concentrations shows initial
of water does concentrations
not appear in (concentrations
the before the acid
expression ionizes),
for the changes in
equilibrium concentration,
constant, so and
we do not equilibrium
need to concentrations
consider its follows (the
change in data given in
concentration the problem
when setting appear in
up the ICE color):
table.

Solve for x and the equilibrium concentrations.

At equilibrium:

Equation:

$$K_a = 1.8 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_2^-]}{[\text{HCO}_2\text{H}]} = \frac{(x)(x)}{0.534 - x} = 1.8 \times 10^{-4}$$

Equation:

Now solve for x . Because the initial concentration of acid is reasonably large and K_a is very small, we assume that $x \ll 0.534$, which *permits* us to simplify the denominator term as $(0.534 - x) = 0.534$. This gives:

Equation:

$$K_a = 1.8 \times 10^{-4} = \frac{x^2}{0.534}$$

Solve for x as follows:

Equation:

$$x^2 = 0.534 \times (1.8 \times 10^{-4}) = 9.6 \times 10^{-5}$$

Equation:

$$x = \sqrt{9.6 \times 10^{-5}}$$

Equation:

$$= 9.8 \times 10^{-3}$$

To check the assumption that x is small compared to 0.534, we calculate:

Equation:

$$\frac{x}{0.534} = \frac{9.8 \times 10^{-3}}{0.534} = 1.8 \times 10^{-2} \text{ (1.8\% of 0.534)}$$

x is less than 5% of the initial concentration; the assumption is valid.

We find the equilibrium concentration of hydronium ion in this formic acid solution from its initial concentration and the change in that concentration as indicated in the last line of the table:

Equation:

$$[\text{H}_3\text{O}^+] = \sim 0 + x = 0 + 9.8 \times 10^{-3} M.$$

Equation:

$$= 9.8 \times 10^{-3} M$$

The pH of the solution can be found by taking the negative log of the $[\text{H}_3\text{O}^+]$, so:

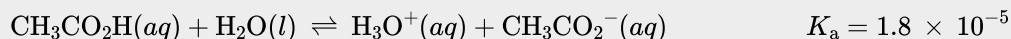
Equation:

$$-\log(9.8 \times 10^{-3}) = 2.01$$

Check Your Learning

Only a small fraction of a weak acid ionizes in aqueous solution. What is the percent ionization of acetic acid in a 0.100-M solution of acetic acid, $\text{CH}_3\text{CO}_2\text{H}$?

Equation:



(Hint: Determine $[\text{CH}_3\text{CO}_2^-]$ at equilibrium.) Recall that the percent ionization is the fraction of acetic acid that is ionized $\times 100$, or $\frac{[\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]_{\text{initial}}} \times 100$.

Note:

Answer:

percent ionization = 1.3%

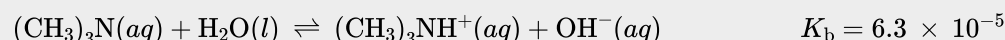
The following example shows that the concentration of products produced by the ionization of a weak base can be determined by the same series of steps used with a weak acid.

Example:

Equilibrium Concentrations in a Solution of a Weak Base

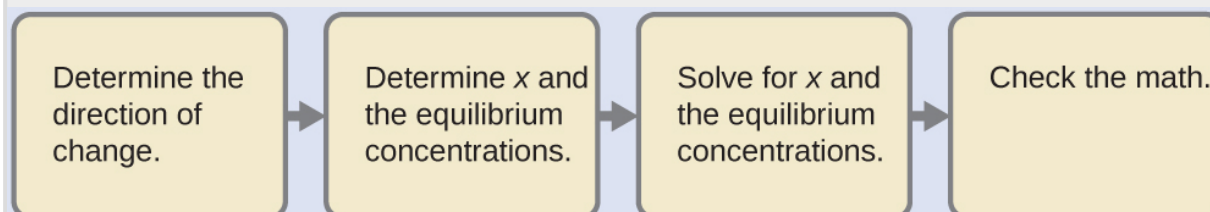
Find the concentration of hydroxide ion in a 0.25-M solution of trimethylamine, a weak base:

Equation:



Solution

This problem requires that we calculate an equilibrium concentration by determining concentration changes as the ionization of a base goes to equilibrium. The solution is approached in the same way as that for the ionization of formic acid in [\[link\]](#). The reactants and products will be different and the numbers will be different, but the logic will be the same:



Determine x and equilibrium concentrations

. The table shows the changes and concentrations:

	$(\text{CH}_3)_3\text{N} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_3\text{NH}^+ + \text{OH}^-$			
Initial concentration (M)	0.25		0	~0
Change (M)	-x		x	x
Equilibrium concentration (M)	$0.25 + (-x)$		$0 + x$	$\sim 0 + x$

Solve for x and the equilibrium concentrations

. At equilibrium:

Equation:

$$K_b = \frac{[(\text{CH}_3)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3)_3\text{N}]} = \frac{(x)(x)}{0.25 - x} = 6.3 \times 10^{-5}$$

If we assume x is small relative to 0.25, then we can replace (0.25 - x) in the preceding equation with 0.25. Solving the simplified equation gives:

Check the work. A check of our arithmetic shows that $K_b = 6.3 \times 10^{-5}$.

Check Your Learning

(a) Show that the calculation in Step 2 of this example gives an x of 4.0×10^{-3} and the calculation in Step 3 shows $K_b = 6.3 \times 10^{-5}$.

(b) Find the concentration of hydroxide ion in a 0.0325-M solution of ammonia, a weak base with a K_b of 1.76×10^{-5} . Calculate the percent ionization of ammonia, the fraction ionized $\times 100$, or $\frac{[\text{NH}_4^+]}{[\text{NH}_3]} \times 100$

Note:

Answer:

$7.56 \times 10^{-4} \text{ M}$, 2.33%

Some weak acids and weak bases ionize to such an extent that the simplifying assumption that x is small relative to the initial concentration of the acid or base is inappropriate. As we solve for the equilibrium concentrations in such cases, we will see that we cannot neglect the change in the initial concentration of the acid or base, and we must solve the equilibrium equations by using the quadratic equation.

Example:

Equilibrium Concentrations in a Solution of a Weak Acid

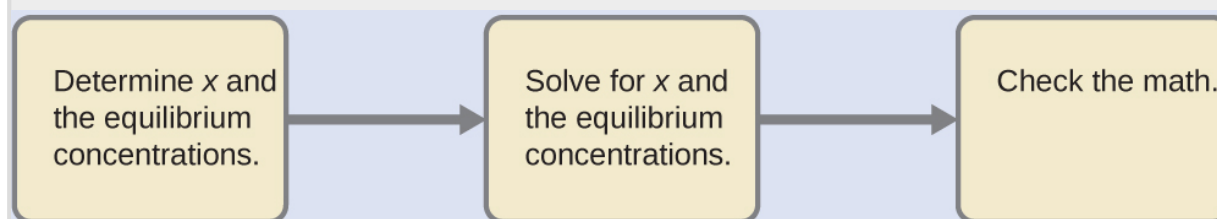
Sodium bisulfate, NaHSO_4 , is used in some household cleansers because it contains the HSO_4^- ion, a weak acid. What is the pH of a 0.50-M solution of HSO_4^- ?

Equation:



Solution

We need to determine the equilibrium concentration of the hydronium ion that results from the ionization of HSO_4^- so that we can use $[\text{H}_3\text{O}^+]$ to determine the pH. As in the previous examples, we can approach the solution by the following steps:



Determine x and equilibrium concentrations

. This table shows the changes and concentrations:

	HSO_4^-	+	H_2O	\rightleftharpoons	H_3O^+	+	SO_4^{2-}
Initial concentration (M)	0.50				~ 0		0
Change (M)	$-x$				x		x
Equilibrium concentration (M)	$0.50 + (-x) = 0.50 - x$				$0 + x = x$		$0 + x = x$

Solve for x and the equilibrium concentrations

. As x , we will find x . At this is more complicated than in previous examples. As we begin solving for equilibrium:

Equation:

$$K_a = 1.2 \times 10^{-2} = \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \frac{(x)(x)}{0.50 - x}$$

If we assume a that

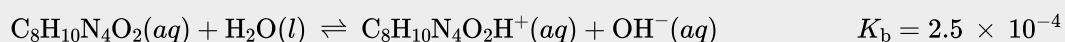
we discuss
these
complications
we should not
lose track of
the fact that it
is still the
purpose of
this step to
determine the
value of

Check Your Learning

(a) Show that the quadratic formula gives $x = 7.2 \times 10^{-2}$.

(b) Calculate the pH in a 0.010-M solution of caffeine, a weak base:

Equation:



(Hint: It will be necessary to convert $[\text{OH}^-]$ to $[\text{H}_3\text{O}^+]$ or pOH to pH toward the end of the calculation.)

Note:

Answer:

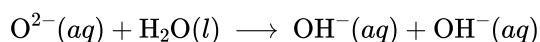
pH 11.16

The Relative Strengths of Strong Acids and Bases

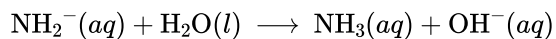
Strong acids, such as HCl, HBr, and HI, all exhibit the same strength in water. The water molecule is such a strong base compared to the conjugate bases Cl^- , Br^- , and I^- that ionization of these strong acids is essentially complete in aqueous solutions. In solvents less basic than water, we find HCl, HBr, and HI differ markedly in their tendency to give up a proton to the solvent. For example, when dissolved in ethanol (a weaker base than water), the extent of ionization increases in the order $\text{HCl} < \text{HBr} < \text{HI}$, and so HI is demonstrated to be the strongest of these acids. The inability to discern differences in strength among strong acids dissolved in water is known as the **leveling effect of water**.

Water also exerts a leveling effect on the strengths of strong bases. For example, the oxide ion, O^{2-} , and the amide ion, NH_2^- , are such strong bases that they react completely with water:

Equation:



Equation:



Thus, O^{2-} and NH_2^- appear to have the same base strength in water; they both give a 100% yield of hydroxide ion.

Effect of Molecular Structure on Acid-Base Strength

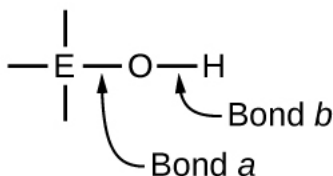
In the absence of any leveling effect, the acid strength of binary compounds of hydrogen with nonmetals (A) increases as the H-A bond strength decreases down a group in the periodic table. For group 17, the order of increasing acidity is $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$. Likewise, for group 16, the order of increasing acid strength is $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$.

Across a row in the periodic table, the acid strength of binary hydrogen compounds increases with increasing electronegativity of the nonmetal atom because the polarity of the H-A bond increases. Thus, the order of increasing acidity (for removal of one proton) across the second row is $\text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O} < \text{HF}$; across the third row, it is $\text{SiH}_4 < \text{PH}_3 < \text{H}_2\text{S} < \text{HCl}$ (see [link](#)).

14	15	16	17	
6 CH₄ Neither acid nor base	7 NH₃ Weak base $K_b = 1.8 \times 10^{-5}$	8 H₂O Neutral	9 HF Weak acid $K_a = 6.8 \times 10^{-4}$	<div>Increasing acid strength</div> <div>Increasing base strength</div>
14 SiH₄ Neither acid nor base	15 PH₃ Very weak base $K_b = 4 \times 10^{-28}$	16 H₂S Weak acid $K_a = 9.5 \times 10^{-8}$	17 HCl Strong acid	
<div>Increasing acid strength</div> <div>Increasing base strength</div>				

As you move from left to right and down the periodic table, the acid strength increases. As you move from right to left and up, the base strength increases.

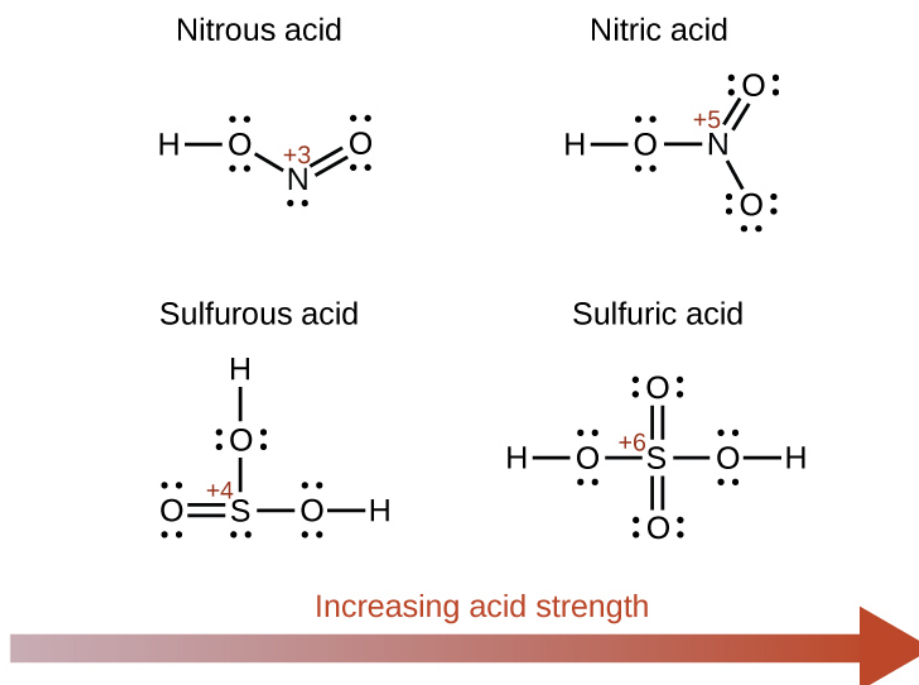
Compounds containing oxygen and one or more hydroxyl (OH) groups can be acidic, basic, or amphoteric, depending on the position in the periodic table of the central atom E, the atom bonded to the hydroxyl group. Such compounds have the general formula $\text{O}_n\text{E}(\text{OH})_m$, and include sulfuric acid, $\text{O}_2\text{S}(\text{OH})_2$, sulfurous acid, $\text{OS}(\text{OH})_2$, nitric acid, O_2NOH , perchloric acid, O_3ClOH , aluminum hydroxide, $\text{Al}(\text{OH})_3$, calcium hydroxide, $\text{Ca}(\text{OH})_2$, and potassium hydroxide, KOH :



If the central atom, E, has a low electronegativity, its attraction for electrons is low. Little tendency exists for the central atom to form a strong covalent bond with the oxygen atom, and bond *a* between the element and oxygen is more readily broken than bond *b* between oxygen and hydrogen. Hence bond *a* is ionic, hydroxide ions are released to the solution, and the material behaves as a base—this is the case with $\text{Ca}(\text{OH})_2$ and KOH . Lower electronegativity is characteristic of the more metallic elements; hence, the metallic elements form ionic hydroxides that are by definition basic compounds.

If, on the other hand, the atom E has a relatively high electronegativity, it strongly attracts the electrons it shares with the oxygen atom, making bond *a* relatively strongly covalent. The oxygen-hydrogen bond, bond *b*, is thereby weakened because electrons are displaced toward E. Bond *b* is polar and readily releases hydrogen ions to the solution, so the material behaves as an acid. High electronegativities are characteristic of the more nonmetallic elements. Thus, nonmetallic elements form covalent compounds containing acidic $-\text{OH}$ groups that are called **oxyacids**.

Increasing the oxidation number of the central atom E also increases the acidity of an oxyacid because this increases the attraction of E for the electrons it shares with oxygen and thereby weakens the O-H bond. Sulfuric acid, H_2SO_4 , or $\text{O}_2\text{S}(\text{OH})_2$ (with a sulfur oxidation number of +6), is more acidic than sulfurous acid, H_2SO_3 , or $\text{OS}(\text{OH})_2$ (with a sulfur oxidation number of +4). Likewise nitric acid, HNO_3 , or O_2NOH (N oxidation number = +5), is more acidic than nitrous acid, HNO_2 , or ONOH (N oxidation number = +3). In each of these pairs, the oxidation number of the central atom is larger for the stronger acid ([link](#)).

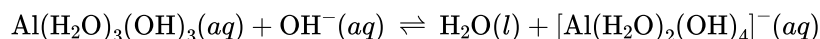


As the oxidation number of the central atom E increases, the acidity also increases.

Hydroxy compounds of elements with intermediate electronegativities and relatively high oxidation numbers (for example, elements near the diagonal line separating the metals from the nonmetals in the periodic table) are usually amphoteric. This means that the hydroxy compounds act as acids when they react with strong bases and as bases when they react with strong acids. The amphoterism of aluminum hydroxide, which commonly exists as the hydrate $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3$, is reflected in its solubility in both strong acids and strong bases. In strong bases, the

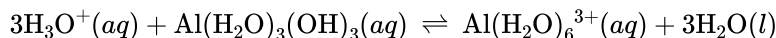
relatively insoluble hydrated aluminum hydroxide, $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3$, is converted into the soluble ion, $[\text{Al}(\text{H}_2\text{O})_2(\text{OH})_4]^-$, by reaction with hydroxide ion:

Equation:



In this reaction, a proton is transferred from one of the aluminum-bound H_2O molecules to a hydroxide ion in solution. The $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3$ compound thus acts as an acid under these conditions. On the other hand, when dissolved in strong acids, it is converted to the soluble ion $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ by reaction with hydronium ion:

Equation:



In this case, protons are transferred from hydronium ions in solution to $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3$, and the compound functions as a base.

Key Concepts and Summary

The strengths of Brønsted-Lowry acids and bases in aqueous solutions can be determined by their acid or base ionization constants. Stronger acids form weaker conjugate bases, and weaker acids form stronger conjugate bases. Thus strong acids are completely ionized in aqueous solution because their conjugate bases are weaker bases than water. Weak acids are only partially ionized because their conjugate bases are strong enough to compete successfully with water for possession of protons. Strong bases react with water to quantitatively form hydroxide ions. Weak bases give only small amounts of hydroxide ion. The strengths of the binary acids increase from left to right across a period of the periodic table ($\text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O} < \text{HF}$), and they increase down a group ($\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$). The strengths of oxyacids that contain the same central element increase as the oxidation number of the element increases ($\text{H}_2\text{SO}_3 < \text{H}_2\text{SO}_4$). The strengths of oxyacids also increase as the electronegativity of the central element increases [$\text{H}_2\text{SeO}_4 < \text{H}_2\text{SO}_4$].

Key Equations

- $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$
- $K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$
- $K_a \times K_b = 1.0 \times 10^{-14} = K_w$
- Percent ionization = $\frac{[\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{HA}]_0} \times 100$

Chemistry End of Chapter Exercises

Exercise:

Problem:

Explain why the neutralization reaction of a strong acid and a weak base gives a weakly acidic solution.

Exercise:

Problem:

Explain why the neutralization reaction of a weak acid and a strong base gives a weakly basic solution.

Solution:

The salt ionizes in solution, but the anion slightly reacts with water to form the weak acid. This reaction also forms OH^- , which causes the solution to be basic.

Exercise:

Problem:

Use this list of important industrial compounds (and [link](#)) to answer the following questions regarding: CaO , $\text{Ca}(\text{OH})_2$, $\text{CH}_3\text{CO}_2\text{H}$, CO_2 , HCl , H_2CO_3 , HF , HNO_2 , HNO_3 , H_3PO_4 , H_2SO_4 , NH_3 , NaOH , Na_2CO_3 .

- (a) Identify the strong Brønsted-Lowry acids and strong Brønsted-Lowry bases.
- (b) List those compounds in (a) that can behave as Brønsted-Lowry acids with strengths lying between those of H_3O^+ and H_2O .
- (c) List those compounds in (a) that can behave as Brønsted-Lowry bases with strengths lying between those of H_2O and OH^- .

Exercise:

Problem:

The odor of vinegar is due to the presence of acetic acid, $\text{CH}_3\text{CO}_2\text{H}$, a weak acid. List, in order of descending concentration, all of the ionic and molecular species present in a 1-*M* aqueous solution of this acid.

Solution:



Exercise:

Problem:

Household ammonia is a solution of the weak base NH_3 in water. List, in order of descending concentration, all of the ionic and molecular species present in a 1-*M* aqueous solution of this base.

Exercise:

Problem:

Explain why the ionization constant, K_a , for H_2SO_4 is larger than the ionization constant for H_2SO_3 .

Solution:

The oxidation state of the sulfur in H_2SO_4 is greater than the oxidation state of the sulfur in H_2SO_3 .

Exercise:

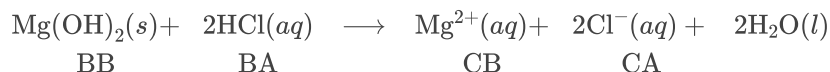
Problem: Explain why the ionization constant, K_a , for HI is larger than the ionization constant for HF .

Exercise:

Problem:

Gastric juice, the digestive fluid produced in the stomach, contains hydrochloric acid, HCl . Milk of Magnesia, a suspension of solid $\text{Mg}(\text{OH})_2$ in an aqueous medium, is sometimes used to neutralize excess stomach acid. Write a complete balanced equation for the neutralization reaction, and identify the conjugate acid-base pairs.

Solution:



Exercise:**Problem:**

Nitric acid reacts with insoluble copper(II) oxide to form soluble copper(II) nitrate, $\text{Cu}(\text{NO}_3)_2$, a compound that has been used to prevent the growth of algae in swimming pools. Write the balanced chemical equation for the reaction of an aqueous solution of HNO_3 with CuO .

Exercise:**Problem:**

What is the ionization constant at 25 °C for the weak acid CH_3NH_3^+ , the conjugate acid of the weak base CH_3NH_2 , $K_b = 4.4 \times 10^{-4}$.

Solution:

$$K_a = 2.3 \times 10^{-11}$$

Exercise:**Problem:**

What is the ionization constant at 25 °C for the weak acid $(\text{CH}_3)_2\text{NH}_2^+$, the conjugate acid of the weak base $(\text{CH}_3)_2\text{NH}$, $K_b = 5.9 \times 10^{-4}$?

Exercise:**Problem:**

Which base, CH_3NH_2 or $(\text{CH}_3)_2\text{NH}$, is the stronger base? Which conjugate acid, $(\text{CH}_3)_2\text{NH}_2^+$ or $(\text{CH}_3)_2\text{NH}_3^+$, is the stronger acid?

Solution:

The stronger base or stronger acid is the one with the larger K_b or K_a , respectively. In these two examples, they are $(\text{CH}_3)_2\text{NH}$ and CH_3NH_3^+ .

Exercise:

Problem: Which is the stronger acid, NH_4^+ or HBrO ?

Exercise:

Problem: Which is the stronger base, $(\text{CH}_3)_3\text{N}$ or H_2BO_3^- ?

Solution:

triethylamine.

Exercise:**Problem:**

Predict which acid in each of the following pairs is the stronger and explain your reasoning for each.

(a) H_2O or HF

(b) $\text{B}(\text{OH})_3$ or $\text{Al}(\text{OH})_3$

(c) HSO_3^- or HSO_4^-

(d) NH_3 or H_2S

(e) H_2O or H_2Te

Exercise:

Problem:

Predict which compound in each of the following pairs of compounds is more acidic and explain your reasoning for each.

(a) HSO_4^- or HSeO_4^-

(b) NH_3 or H_2O

(c) PH_3 or HI

(d) NH_3 or PH_3

(e) H_2S or HBr

Solution:

(a) HSO_4^- ; higher electronegativity of the central ion. (b) H_2O ; NH_3 is a base and water is neutral, or decide on the basis of K_a values. (c) HI ; PH_3 is weaker than HCl ; HCl is weaker than HI . Thus, PH_3 is weaker than HI . (d) PH_3 ; in binary compounds of hydrogen with nonmetals, the acidity increases for the element lower in a group. (e) HBr ; in a period, the acidity increases from left to right; in a group, it increases from top to bottom. Br is to the left and below S, so HBr is the stronger acid.

Exercise:

Problem:

Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.

(a) acidity: HCl , HBr , HI

(b) basicity: H_2O , OH^- , H^- , Cl^-

(c) basicity: $\text{Mg}(\text{OH})_2$, $\text{Si}(\text{OH})_4$, $\text{ClO}_3(\text{OH})$ (Hint: Formula could also be written as HClO_4).

(d) acidity: HF , H_2O , NH_3 , CH_4

Exercise:

Problem:

Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.

(a) acidity: NaHSO_3 , NaHSeO_3 , NaHSO_4

(b) basicity: BrO_2^- , ClO_2^- , IO_2^-

(c) acidity: HOCl , HOBr , HOI

(d) acidity: HOCl , HOClO , HOClO_2 , HOClO_3

(e) basicity: NH_2^- , HS^- , HTe^- , PH_2^-

(f) basicity: BrO^- , BrO_2^- , BrO_3^- , BrO_4^-

Solution:

(a) $\text{NaHSeO}_3 < \text{NaHSO}_3 < \text{NaHSO}_4$; in polyoxy acids, the more electronegative central element—S, in this case—forms the stronger acid. The larger number of oxygen atoms on the central atom (giving it a higher oxidation state) also creates a greater release of hydrogen atoms, resulting in a stronger acid. As a salt, the acidity increases in the same manner. (b) $\text{ClO}_2^- < \text{BrO}_2^- < \text{IO}_2^-$; the basicity of the anions in a series of acids will be the opposite of the acidity in their oxyacids. The acidity increases as the electronegativity of the central atom increases. Cl is more electronegative than Br, and I is the least electronegative of the three. (c) $\text{HOI} < \text{HOBr} < \text{HOCl}$; in a series of the same form of oxyacids, the acidity increases as the electronegativity of the central atom increases. Cl is more electronegative than Br, and I is the least electronegative of the three. (d) $\text{HOCl} < \text{HOClO} < \text{HOClO}_2 < \text{HOClO}_3$; in a series of oxyacids of the same central element, the acidity increases as the number of oxygen atoms increases (or as the oxidation state of the central atom increases). (e) $\text{HTe}^- < \text{HS}^- < \text{PH}_2^- < \text{NH}_2^-$; PH_2^- and NH_2^- are anions of weak bases, so they act as strong bases toward H^+ . HTe^- and HS^- are anions of weak acids, so they have less basic character. In a periodic group, the more electronegative element has the more basic anion. (f) $\text{BrO}_4^- < \text{BrO}_3^- < \text{BrO}_2^- < \text{BrO}^-$; with a larger number of oxygen atoms (that is, as the oxidation state of the central ion increases), the corresponding acid becomes more acidic and the anion consequently less basic.

Exercise:

Problem:

Both HF and HCN ionize in water to a limited extent. Which of the conjugate bases, F^- or CN^- , is the stronger base? See [\[link\]](#).

Exercise:

Problem:

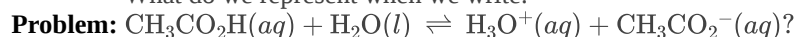
The active ingredient formed by aspirin in the body is salicylic acid, $\text{C}_6\text{H}_4\text{OH}(\text{CO}_2\text{H})$. The carboxyl group ($-\text{CO}_2\text{H}$) acts as a weak acid. The phenol group (an OH group bonded to an aromatic ring) also acts as an acid but a much weaker acid. List, in order of descending concentration, all of the ionic and molecular species present in a 0.001-*M* aqueous solution of $\text{C}_6\text{H}_4\text{OH}(\text{CO}_2\text{H})$.

Solution:



Exercise:

What do we represent when we write:



Exercise:

Problem:

Explain why equilibrium calculations are not necessary to determine ionic concentrations in solutions of certain strong electrolytes such as NaOH and HCl. Under what conditions are equilibrium calculations necessary as part of the determination of the concentrations of all ions of some other strong electrolytes in solution?

Solution:

Strong electrolytes are 100% ionized, and, as long as the component ions are neither weak acids nor weak bases, the ionic species present result from the dissociation of the strong electrolyte. Equilibrium calculations are necessary when one (or more) of the ions is a weak acid or a weak base.

Exercise:

Problem:

Are the concentrations of hydronium ion and hydroxide ion in a solution of an acid or a base in water directly proportional or inversely proportional? Explain your answer.

Exercise:**Problem:**

What two common assumptions can simplify calculation of equilibrium concentrations in a solution of a weak acid?

Solution:

1. Assume that the change in initial concentration of the acid as the equilibrium is established can be neglected, so this concentration can be assumed constant and equal to the initial value of the total acid concentration. 2. Assume we can neglect the contribution of water to the equilibrium concentration of H_3O^+ .

Exercise:**Problem:**

What two common assumptions can simplify calculation of equilibrium concentrations in a solution of a weak base?

Exercise:**Problem:**

Which of the following will increase the percent of NH_3 that is converted to the ammonium ion in water (Hint: Use LeChâtelier's principle.)?

- (a) addition of NaOH
 - (b) addition of HCl
 - (c) addition of NH_4Cl
-

Solution:

- (b) The addition of HCl

Exercise:**Problem:**

Which of the following will increase the percent of HF that is converted to the fluoride ion in water?

- (a) addition of NaOH
- (b) addition of HCl
- (c) addition of NaF

Exercise:**Problem:**

What is the effect on the concentrations of NO_2^- , HNO_2 , and OH^- when the following are added to a solution of KNO_2 in water:

- (a) HCl

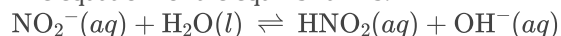
(b) HNO_2

(c) NaOH

(d) NaCl

(e) KNO

The equation for the equilibrium is:



Solution:

(a) Adding HCl will add H_3O^+ ions, which will then react with the OH^- ions, lowering their concentration. The equilibrium will shift to the right, increasing the concentration of HNO_2 , and decreasing the concentration of NO_2^- ions. (b) Adding HNO_2 increases the concentration of HNO_2 and shifts the equilibrium to the left, increasing the concentration of NO_2^- ions and decreasing the concentration of OH^- ions. (c) Adding NaOH adds OH^- ions, which shifts the equilibrium to the left, increasing the concentration of NO_2^- ions and decreasing the concentrations of HNO_2 . (d) Adding NaCl has no effect on the concentrations of the ions. (e) Adding KNO_2 adds NO_2^- ions and shifts the equilibrium to the right, increasing the HNO_2 and OH^- ion concentrations.

Exercise:

Problem:

What is the effect on the concentration of hydrofluoric acid, hydronium ion, and fluoride ion when the following are added to separate solutions of hydrofluoric acid?

(a) HCl

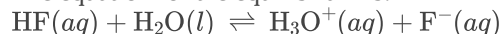
(b) KF

(c) NaCl

(d) KOH

(e) HF

The equation for the equilibrium is:



Exercise:

Problem:

Why is the hydronium ion concentration in a solution that is 0.10 M in HCl and 0.10 M in HCOOH determined by the concentration of HCl ?

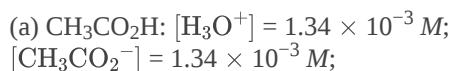
Solution:

This is a case in which the solution contains a mixture of acids of different ionization strengths. In solution, the HCO_2H exists primarily as HCO_2H molecules because the ionization of the weak acid is suppressed by the strong acid. Therefore, the HCO_2H contributes a negligible amount of hydronium ions to the solution. The stronger acid, HCl , is the dominant producer of hydronium ions because it is completely ionized. In such a solution, the stronger acid determines the concentration of hydronium ions, and the ionization of the weaker acid is fixed by the $[\text{H}_3\text{O}^+]$ produced by the stronger acid.

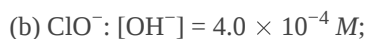
Exercise:

Problem:

From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.



$$[\text{CH}_3\text{CO}_2\text{H}] = 9.866 \times 10^{-2} \text{ M};$$



$$[\text{HClO}] = 2.38 \times 10^{-5} \text{ M};$$

$$[\text{ClO}^-] = 0.273 \text{ M};$$



$$[\text{H}_3\text{O}^+] = 9.8 \times 10^{-3} \text{ M};$$

$$[\text{HCO}_2^-] = 9.8 \times 10^{-3} \text{ M};$$

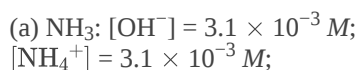


$$[\text{C}_6\text{H}_5\text{NH}_2] = 2.3 \times 10^{-3} \text{ M};$$

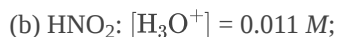
$$[\text{H}_3\text{O}^+] = 2.3 \times 10^{-3} \text{ M}$$

Exercise:**Problem:**

From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.



$$[\text{NH}_3] = 0.533 \text{ M};$$



$$[\text{NO}_2^-] = 0.0438 \text{ M};$$

$$[\text{HNO}_2] = 1.07 \text{ M};$$



$$[(\text{CH}_3)_3\text{NH}^+] = 4.3 \times 10^{-3} \text{ M};$$

$$[\text{OH}^-] = 4.3 \times 10^{-3} \text{ M};$$



$$[\text{NH}_3] = 7.5 \times 10^{-6} \text{ M};$$

$$[\text{H}_3\text{O}^+] = 7.5 \times 10^{-6} \text{ M}$$

Solution:

(a) $K_b = 1.8 \times 10^{-5}$;

(b) $K_a = 4.5 \times 10^{-4}$;

(c) $K_b = 7.4 \times 10^{-5}$;

(d) $K_a = 5.6 \times 10^{-10}$

Exercise:

Problem: Determine K_b for the nitrite ion, NO_2^- . In a 0.10- M solution this base is 0.0015% ionized.

Exercise:

Problem: Determine K_a for hydrogen sulfate ion, HSO_4^- . In a 0.10- M solution the acid is 29% ionized.

Solution:

$$K_a = 1.2 \times 10^{-2}$$

Exercise:**Problem:**

Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:

- (a) F^-
- (b) NH_4^+
- (c) AsO_4^{3-}
- (d) $(\text{CH}_3)_2\text{NH}_2^+$
- (e) NO_2^-
- (f) HC_2O_4^- (as a base)

Exercise:**Problem:**

Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:

- (a) HTe^- (as a base)
 - (b) $(\text{CH}_3)_3\text{NH}^+$
 - (c) HAsO_4^{3-} (as a base)
 - (d) HO_2^- (as a base)
 - (e) $\text{C}_6\text{H}_5\text{NH}_3^+$
 - (f) HSO_3^- (as a base)
-

Solution:

- (a) $K_b = 4.3 \times 10^{-12}$;
- (b) $K_a = 1.6 \times 10^{-8}$;
- (c) $K_b = 5.9 \times 10^{-7}$;
- (d) $K_b = 4.2 \times 10^{-3}$;
- (e) $K_b = 2.3 \times 10^{-3}$;
- (f) $K_b = 6.3 \times 10^{-13}$

Exercise:

Problem:

For which of the following solutions must we consider the ionization of water when calculating the pH or pOH?

- (a) $3 \times 10^{-8} \text{ M HNO}_3$
- (b) 0.10 g HCl in 1.0 L of solution
- (c) 0.00080 g NaOH in 0.50 L of solution
- (d) $1 \times 10^{-7} \text{ M Ca(OH)}_2$
- (e) 0.0245 M KNO₃

Exercise:**Problem:**

Even though both NH₃ and C₆H₅NH₂ are weak bases, NH₃ is a much stronger base than C₆H₅NH₂. Which of the following is correct at equilibrium for a solution that is initially 0.10 M in NH₃ and 0.10 M in C₆H₅NH₂?

- (a) $[\text{OH}^-] = [\text{NH}_4^+]$
- (b) $[\text{NH}_4^+] = [\text{C}_6\text{H}_5\text{NH}_3^+]$
- (c) $[\text{OH}^-] = [\text{C}_6\text{H}_5\text{NH}_3^+]$
- (d) $[\text{NH}_3] = [\text{C}_6\text{H}_5\text{NH}_2]$
- (e) both a and b are correct

Solution:

(a) is the correct statement.

Exercise:**Problem:**

Calculate the equilibrium concentration of the nonionized acids and all ions in a solution that is 0.25 M in HCO₂H and 0.10 M in HClO.

Exercise:**Problem:**

Calculate the equilibrium concentration of the nonionized acids and all ions in a solution that is 0.134 M in HNO₂ and 0.120 M in HBrO.

Solution:

$$\begin{aligned}[\text{H}_3\text{O}^+] &= 7.5 \times 10^{-3} \text{ M} \\[\text{HNO}_2] &= 0.127 \\[\text{OH}^-] &= 1.3 \times 10^{-12} \text{ M} \\[\text{BrO}^-] &= 4.5 \times 10^{-8} \text{ M} \\[\text{HBrO}] &= 0.120 \text{ M}\end{aligned}$$

Exercise:

Problem:

Calculate the equilibrium concentration of the nonionized bases and all ions in a solution that is 0.25 M in CH_3NH_2 and 0.10 M in $\text{C}_5\text{H}_5\text{N}$ ($K_b = 1.7 \times 10^{-9}$).

Exercise:**Problem:**

Calculate the equilibrium concentration of the nonionized bases and all ions in a solution that is 0.115 M in NH_3 and 0.100 M in $\text{C}_6\text{H}_5\text{NH}_2$.

Solution:

$$[\text{OH}^-] = [\text{NO}_4^+] = 0.0014 \text{ M}$$

$$[\text{NH}_3] = 0.144 \text{ M}$$

$$[\text{H}_3\text{O}^+] = 6.9 \times 10^{-12} \text{ M}$$

$$[\text{C}_6\text{H}_5\text{NH}_3^+] = 3.9 \times 10^{-8} \text{ M}$$

$$[\text{C}_6\text{H}_5\text{NH}_2] = 0.100 \text{ M}$$

Exercise:

Problem: Using the K_a value of 1.4×10^{-5} , place $\text{Al}(\text{H}_2\text{O})_6^{3+}$ in the correct location in [\[link\]](#).

Exercise:**Problem:**

Calculate the concentration of all solute species in each of the following solutions of acids or bases. Assume that the ionization of water can be neglected, and show that the change in the initial concentrations can be neglected. Ionization constants can be found in [Appendix H](#) and [Appendix I](#).

(a) 0.0092 M HClO , a weak acid

(b) 0.0784 M $\text{C}_6\text{H}_5\text{NH}_2$, a weak base

(c) 0.0810 M HCN , a weak acid

(d) 0.11 M $(\text{CH}_3)_3\text{N}$, a weak base

(e) 0.120 M $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ a weak acid, $K_a = 1.6 \times 10^{-7}$

Solution:

$$(a) \frac{[\text{H}_3\text{O}^+][\text{ClO}^-]}{[\text{HClO}]} = \frac{(x)(x)}{(0.0092-x)} \approx \frac{(x)(x)}{0.0092} = 2.9 \times 10^{-8}$$

Solving for x gives $1.63 \times 10^{-5} \text{ M}$. This value is less than 5% of 0.0092, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$$[\text{H}_3\text{O}^+] = [\text{ClO}^-] = 5.8 \times 10^{-5} \text{ M}$$

$$[\text{HClO}] = 0.00092 \text{ M}$$

$$[\text{OH}^-] = 6.1 \times 10^{-10} \text{ M};$$

$$(b) \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]} = \frac{(x)(x)}{(0.0784-x)} \approx \frac{(x)(x)}{0.0784} = 4.3 \times 10^{-10}$$

Solving for x gives $5.81 \times 10^{-6} \text{ M}$. This value is less than 5% of 0.0784, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$$[\text{CH}_3\text{CO}_2^-] = [\text{OH}^-] = 5.8 \times 10^{-6} \text{ M}$$

$$[\text{C}_6\text{H}_5\text{NH}_2] = 0.00784$$

$$[\text{H}_3\text{O}^+] = 1.7 \times 10^{-9} \text{ M};$$

$$(c) \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]} = \frac{(x)(x)}{(0.0810-x)} \approx \frac{(x)(x)}{0.0810} = 4.9 \times 10^{-10}$$

Solving for x gives $6.30 \times 10^{-6} M$. This value is less than 5% of 0.0810, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$$[\text{H}_3\text{O}^+] = [\text{CN}^-] = 6.3 \times 10^{-6} M$$

$$[\text{HCN}] = 0.0810 M$$

$$[\text{OH}^-] = 1.6 \times 10^{-9} M;$$

$$(d) \frac{[(\text{CH}_3)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3)_3\text{N}]} = \frac{(x)(x)}{(0.11-x)} \approx \frac{(x)(x)}{0.11} = 6.3 \times 10^{-5}$$

Solving for x gives $2.63 \times 10^{-3} M$. This value is less than 5% of 0.11, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$$[(\text{CH}_3)_3\text{NH}^+] = [\text{OH}^-] = 2.6 \times 10^{-3} M$$

$$[(\text{CH}_3)_3\text{N}] = 0.11 M$$

$$[\text{H}_3\text{O}^+] = 3.8 \times 10^{-12} M;$$

$$(e) \frac{[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^+][\text{H}_3\text{O}^+]}{[\text{Fe}(\text{H}_2\text{O})_6^{2+}]} = \frac{(x)(x)}{(0.120-x)} \approx \frac{(x)(x)}{0.120} = 1.6 \times 10^{-7}$$

Solving for x gives $1.39 \times 10^{-4} M$. This value is less than 5% of 0.120, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$$[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^+] = [\text{H}_3\text{O}^+] = 1.4 \times 10^{-4} M$$

$$[\text{Fe}(\text{H}_2\text{O})_6^{2+}] = 0.120 M$$

$$[\text{OH}^-] = 7.2 \times 10^{-11} M$$

Exercise:

Problem:

Propionic acid, $\text{C}_2\text{H}_5\text{CO}_2\text{H}$ ($K_a = 1.34 \times 10^{-5}$), is used in the manufacture of calcium propionate, a food preservative. What is the hydronium ion concentration in a 0.698- M solution of $\text{C}_2\text{H}_5\text{CO}_2\text{H}$?

Exercise:

Problem:

White vinegar is a 5.0% by mass solution of acetic acid in water. If the density of white vinegar is 1.007 g/cm^3 , what is the pH?

Solution:

$$\text{pH} = 2.41$$

Exercise:

Problem:

The ionization constant of lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}$, an acid found in the blood after strenuous exercise, is 1.36×10^{-4} . If 20.0 g of lactic acid is used to make a solution with a volume of 1.00 L, what is the concentration of hydronium ion in the solution?

Exercise:

Problem:

Nicotine, $\text{C}_{10}\text{H}_{14}\text{N}_2$, is a base that will accept two protons ($K_1 = 7 \times 10^{-7}$, $K_2 = 1.4 \times 10^{-11}$). What is the concentration of each species present in a 0.050- M solution of nicotine?

Solution:

$$[\text{C}_{10}\text{H}_{14}\text{N}_2] = 0.049 M$$

$$[\text{C}_{10}\text{H}_{14}\text{N}_2\text{H}^+] = 1.9 \times 10^{-4} M$$

$$[\text{C}_{10}\text{H}_{14}\text{N}_2\text{H}_2^{2+}] = 1.4 \times 10^{-11} M$$

$$[\text{OH}^-] = 1.9 \times 10^{-4} M$$

$$[\text{H}_3\text{O}^+] = 5.3 \times 10^{-11} M$$

Exercise:

Problem: The pH of a 0.20-*M* solution of HF is 1.92. Determine K_a for HF from these data.

Exercise:

Problem: The pH of a 0.15-*M* solution of HSO_4^- is 1.43. Determine K_a for HSO_4^- from these data.

Solution:

$$K_a = 1.2 \times 10^{-2}$$

Exercise:

The pH of a 0.10-*M* solution of caffeine is 11.16. Determine K_b for caffeine from these data:

Problem: $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_8\text{H}_{10}\text{N}_4\text{O}_2\text{H}^+(aq) + \text{OH}^-(aq)$

Exercise:

Problem:

The pH of a solution of household ammonia, a 0.950 *M* solution of NH_3 , is 11.612. Determine K_b for NH_3 from these data.

Solution:

$$K_b = 1.77 \times 10^{-5}$$

Glossary

acid ionization constant (K_a)

equilibrium constant for the ionization of a weak acid

base ionization constant (K_b)

equilibrium constant for the ionization of a weak base

leveling effect of water

any acid stronger than H_3O^+ , or any base stronger than OH^- will react with water to form H_3O^+ , or OH^- , respectively; water acts as a base to make all strong acids appear equally strong, and it acts as an acid to make all strong bases appear equally strong

oxyacid

compound containing a nonmetal and one or more hydroxyl groups

percent ionization

ratio of the concentration of the ionized acid to the initial acid concentration, times 100

Hydrolysis of Salt Solutions

By the end of this section, you will be able to:

- Predict whether a salt solution will be acidic, basic, or neutral
- Calculate the concentrations of the various species in a salt solution
- Describe the process that causes solutions of certain metal ions to be acidic

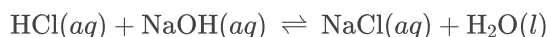
As we have seen in the section on chemical reactions, when an acid and base are mixed, they undergo a neutralization reaction. The word “neutralization” seems to imply that a stoichiometrically equivalent solution of an acid and a base would be neutral. This is sometimes true, but the salts that are formed in these reactions may have acidic or basic properties of their own, as we shall now see.

Acid-Base Neutralization

A solution is neutral when it contains equal concentrations of hydronium and hydroxide ions. When we mix solutions of an acid and a base, an acid-base neutralization reaction occurs. However, even if we mix stoichiometrically equivalent quantities, we may find that the resulting solution is not neutral. It could contain either an excess of hydronium ions or an excess of hydroxide ions because the nature of the salt formed determines whether the solution is acidic, neutral, or basic. The following four situations illustrate how solutions with various pH values can arise following a neutralization reaction using stoichiometrically equivalent quantities:

1. A strong acid and a strong base, such as $\text{HCl}(aq)$ and $\text{NaOH}(aq)$ will react to form a neutral solution since the conjugate partners produced are of negligible strength (see [link](#)):

Equation:



2. A strong acid and a weak base yield a weakly acidic solution. The products of this neutralization reaction are the conjugate base of the strong acid ($K_b \approx 0$, so it doesn't affect pH) and the conjugate acid of the weak base ($K_a > 0$, so it ionizes to make the solution acidic).
3. A weak acid and a strong base yield a weakly basic solution. The products of this neutralization reaction are the conjugate acid of the strong base ($K_a \approx 0$, so it doesn't affect pH) and the conjugate base of the weak acid ($K_b > 0$, so it ionizes to make the solution basic).
4. A weak acid plus a weak base can yield either an acidic or basic solution. This is the most complex of the four types of reactions. When the conjugate acid and the conjugate base are of unequal strengths, the solution can be either acidic or basic, depending on the relative strengths of the two conjugates. To predict whether a particular combination will be acidic or basic, tabulated K values of the conjugates must be compared. (Note: occasionally the weak acid and the weak base can have the same strength, so their respective conjugate base and acid will have the same strength, and the solution will be neutral.)

Note:

Stomach Antacids

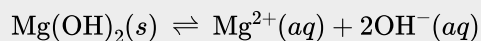
Our stomachs contain a solution of roughly 0.03 M HCl , which helps us digest the food we eat. The burning sensation associated with heartburn is a result of the acid of the stomach leaking through the muscular valve at the top of the stomach into the lower reaches of the esophagus. The lining of the esophagus is not protected from the corrosive effects of stomach acid the way the lining of the stomach is, and the results can be very painful. When we have heartburn, it feels better if we reduce the excess acid in the esophagus by taking an antacid. As you may have guessed, antacids are bases. One of the most common antacids is calcium carbonate, CaCO_3 . The reaction,

Equation:



not only neutralizes stomach acid, it also produces $\text{CO}_2(g)$, which may result in a satisfying belch.

Milk of Magnesia is a suspension of the sparingly soluble base magnesium hydroxide, $\text{Mg}(\text{OH})_2$. It works according to the reaction:

Equation:

The hydroxide ions generated in this equilibrium then go on to react with the hydronium ions from the stomach acid, so that :

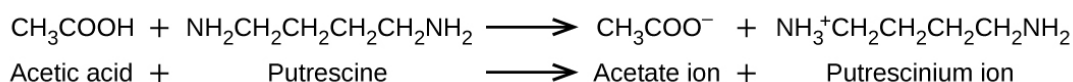
Equation:

This reaction does not produce carbon dioxide, but magnesium-containing antacids can have a laxative effect. Several antacids have aluminum hydroxide, $\text{Al}(\text{OH})_3$, as an active ingredient. The aluminum hydroxide tends to cause constipation, and some antacids use aluminum hydroxide in concert with magnesium hydroxide to balance the side effects of the two substances.

Note:**Culinary Aspects of Chemistry**

Cooking is essentially synthetic chemistry that happens to be safe to eat. There are a number of examples of acid-base chemistry in the culinary world. One example is the use of baking soda, or sodium bicarbonate in baking. NaHCO_3 is a base. When it reacts with an acid such as lemon juice, buttermilk, or sour cream in a batter, bubbles of carbon dioxide gas are formed from decomposition of the resulting carbonic acid, and the batter “rises.” Baking powder is a combination of sodium bicarbonate, and one or more acid salts that react when the two chemicals come in contact with water in the batter.

Many people like to put lemon juice or vinegar, both of which are acids, on cooked fish ([link](#)). It turns out that fish have volatile amines (bases) in their systems, which are neutralized by the acids to yield involatile ammonium salts. This reduces the odor of the fish, and also adds a “sour” taste that we seem to enjoy.



A neutralization reaction takes place between citric acid in lemons or acetic acid in vinegar, and the bases in

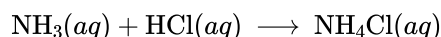
the flesh of fish.

Pickling is a method used to preserve vegetables using a naturally produced acidic environment. The vegetable, such as a cucumber, is placed in a sealed jar submerged in a brine solution. The brine solution favors the growth of beneficial bacteria and suppresses the growth of harmful bacteria. The beneficial bacteria feed on starches in the cucumber and produce lactic acid as a waste product in a process called fermentation. The lactic acid eventually increases the acidity of the brine to a level that kills any harmful bacteria, which require a basic environment. Without the harmful bacteria consuming the cucumbers they are able to last much longer than if they were unprotected. A byproduct of the pickling process changes the flavor of the vegetables with the acid making them taste sour.

Salts of Weak Bases and Strong Acids

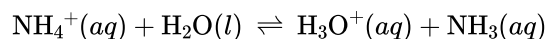
When we neutralize a weak base with a strong acid, the product is a salt containing the conjugate acid of the weak base. This conjugate acid is a weak acid. For example, ammonium chloride, NH_4Cl , is a salt formed by the reaction of the weak base ammonia with the strong acid HCl :

Equation:



A solution of this salt contains ammonium ions and chloride ions. The chloride ion has no effect on the acidity of the solution since HCl is a strong acid. Chloride is a very weak base and will not accept a proton to a measurable extent. However, the ammonium ion, the conjugate acid of ammonia, reacts with water and increases the hydronium ion concentration:

Equation:



The equilibrium equation for this reaction is simply the ionization constant, K_a , for the acid NH_4^+ :

Equation:

$$\frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} = K_a$$

We will not find a value of K_a for the ammonium ion in [Appendix H](#). However, it is not difficult to determine K_a for NH_4^+ from the value of the ionization constant of water, K_w , and K_b , the ionization constant of its conjugate base, NH_3 , using the following relationship:

Equation:

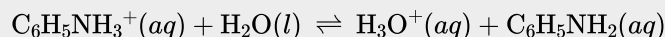
$$K_w = K_a \times K_b$$

This relation holds for any base and its conjugate acid or for any acid and its conjugate base.

Example:

The pH of a Solution of a Salt of a Weak Base and a Strong Acid

Aniline is an amine that is used to manufacture dyes. It is isolated as aniline hydrochloride, $[\text{C}_6\text{H}_5\text{NH}_3^+]\text{Cl}$, a salt prepared by the reaction of the weak base aniline and hydrochloric acid. What is the pH of a 0.233 M solution of aniline hydrochloride?

Equation:**Solution**

The new step in this example is to determine K_a for the $\text{C}_6\text{H}_5\text{NH}_3^+$ ion. The $\text{C}_6\text{H}_5\text{NH}_3^+$ ion is the conjugate acid of a weak base. The value of K_a for this acid is not listed in [Appendix H](#), but we can determine it from the value of K_b for aniline, $\text{C}_6\text{H}_5\text{NH}_2$, which is given as 4.3×10^{-10} ([link](#)) and [Appendix I](#)):

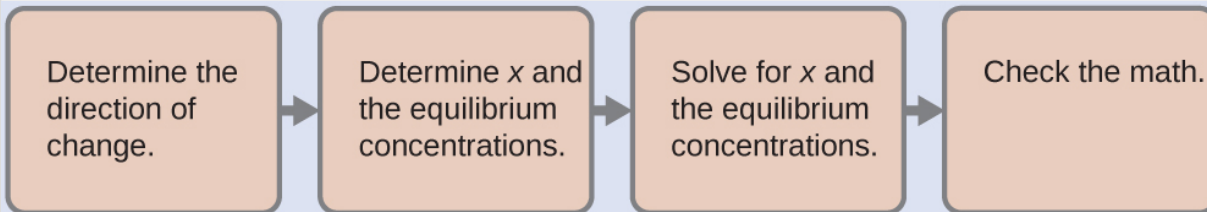
Equation:

$$K_a (\text{for } \text{C}_6\text{H}_5\text{NH}_3^+) \times K_b (\text{for } \text{C}_6\text{H}_5\text{NH}_2) = K_w = 1.0 \times 10^{-14}$$

Equation:

$$K_a (\text{for } \text{C}_6\text{H}_5\text{NH}_3^+) = \frac{K_w}{K_b (\text{for } \text{C}_6\text{H}_5\text{NH}_2)} = \frac{1.0 \times 10^{-14}}{4.3 \times 10^{-10}} = 2.3 \times 10^{-5}$$

Now we have the ionization constant and the initial concentration of the weak acid, the information necessary to determine the equilibrium concentration of H_3O^+ , and the pH:



With these steps we find $[\text{H}_3\text{O}^+] = 2.3 \times 10^{-3} \text{ M}$ and $\text{pH} = 2.64$

Check Your Learning

- (a) Do the calculations and show that the hydronium ion concentration for a 0.233-M solution of $\text{C}_6\text{H}_5\text{NH}_3^+$ is 2.3×10^{-3} and the pH is 2.64.
- (b) What is the hydronium ion concentration in a 0.100-M solution of ammonium nitrate, NH_4NO_3 , a salt composed of the ions NH_4^+ and NO_3^- . Use the data in [link](#) to determine K_b for the ammonium ion. Which is the stronger acid $\text{C}_6\text{H}_5\text{NH}_3^+$ or NH_4^+ ?

Note:**Answer:**

(a) $K_a (\text{for } \text{NH}_4^+) = 5.6 \times 10^{-10}$, $[\text{H}_3\text{O}^+] = 7.5 \times 10^{-6} \text{ M}$; (b) $\text{C}_6\text{H}_5\text{NH}_3^+$ is the stronger acid.

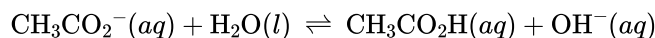
Salts of Weak Acids and Strong Bases

When we neutralize a weak acid with a strong base, we get a salt that contains the conjugate base of the weak acid. This conjugate base is usually a weak base. For example, sodium acetate, NaCH_3CO_2 , is a salt formed by the reaction of the weak acid acetic acid with the strong base sodium hydroxide:

Equation:

A solution of this salt contains sodium ions and acetate ions. The sodium ion has no effect on the acidity of the solution. However, the acetate ion, the conjugate base of acetic acid, reacts with water and increases the concentration of hydroxide ion:

Equation:



The equilibrium equation for this reaction is the ionization constant, K_b , for the base CH_3CO_2^- . The value of K_b can be calculated from the value of the ionization constant of water, K_w , and K_a , the ionization constant of the conjugate acid of the anion using the equation:

Equation:

$$K_w = K_a \times K_b$$

For the acetate ion and its conjugate acid we have:

Equation:

$$K_b (\text{for } \text{CH}_3\text{CO}_2^-) = \frac{K_w}{K_a (\text{for } \text{CH}_3\text{CO}_2\text{H})} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

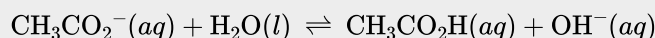
Some handbooks do not report values of K_b . They only report ionization constants for acids. If we want to determine a K_b value using one of these handbooks, we must look up the value of K_a for the conjugate acid and convert it to a K_b value.

Example:

Equilibrium in a Solution of a Salt of a Weak Acid and a Strong Base

Determine the acetic acid concentration in a solution with $[\text{CH}_3\text{CO}_2^-] = 0.050 \text{ M}$ and $[\text{OH}^-] = 2.5 \times 10^{-6} \text{ M}$ at equilibrium. The reaction is:

Equation:



Solution

We are given two of three equilibrium concentrations and asked to find the missing concentration. If we can find the equilibrium constant for the reaction, the process is straightforward.

The acetate ion behaves as a base in this reaction; hydroxide ions are a product. We determine K_b as follows:

Equation:

$$K_b (\text{for } \text{CH}_3\text{CO}_2^-) = \frac{K_w}{K_a (\text{for } \text{CH}_3\text{CO}_2\text{H})} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Now find the missing concentration:

Equation:

$$K_b = \frac{[\text{CH}_3\text{CO}_2\text{H}][\text{OH}^-]}{[\text{CH}_3\text{CO}_2^-]} = 5.6 \times 10^{-10}$$

Equation:

$$= \frac{[\text{CH}_3\text{CO}_2\text{H}](2.5 \times 10^{-6})}{(0.050)} = 5.6 \times 10^{-10}$$

Solving this equation we get $[\text{CH}_3\text{CO}_2\text{H}] = 1.1 \times 10^{-5} \text{ M}$.

Check Your Learning

What is the pH of a 0.083-M solution of CN^- ? Use 4.9×10^{-10} as K_a for HCN. Hint: We will probably need to convert pOH to pH or find $[\text{H}_3\text{O}^+]$ using $[\text{OH}^-]$ in the final stages of this problem.

Note:

Answer:

11.11

Equilibrium in a Solution of a Salt of a Weak Acid and a Weak Base

In a solution of a salt formed by the reaction of a weak acid and a weak base, the salt's cation will be a weak acid (the conjugate acid of the weak base reactant) and its anion will be a weak base (the conjugate base of the weak acid reactant). To predict the pH of the salt solution, we must know both the K_a of the acidic cation and the K_b of the basic anion. If $K_a > K_b$, the solution is acidic, and if $K_b > K_a$, the solution is basic.

Example:

Determining the Acidic or Basic Nature of Salts

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

- (a) KBr
- (b) NaHCO_3
- (c) NH_4Cl
- (d) Na_2HPO_4
- (e) NH_4F

Solution

Consider each of the ions separately in terms of its effect on the pH of the solution, as shown here:

(a) The K^+ cation and the Br^- anion are both spectators, since they are the cation of a strong base (KOH) and the anion of a strong acid (HBr), respectively. The solution is neutral.

(b) The Na^+ cation is a spectator, and will not affect the pH of the solution; while the HCO_3^- anion is amphoteric. The K_a of HCO_3^- is 4.7×10^{-11} , and its K_b is $\frac{1.0 \times 10^{-14}}{4.3 \times 10^{-7}} = 2.3 \times 10^{-8}$.

Since $K_b \gg K_a$, the solution is basic.

(c) The NH_4^+ ion is acidic and the Cl^- ion is a spectator. The solution will be acidic.

(d) The Na^+ cation is a spectator, and will not affect the pH of the solution, while the HPO_4^{2-} anion is amphoteric. The K_a of HPO_4^{2-} is 4.2×10^{-13} , and its K_b is $\frac{1.0 \times 10^{-14}}{6.2 \times 10^{-8}} = 1.6 \times 10^{-7}$. Because $K_b \gg K_a$, the solution is basic.

(e) The NH_4^+ ion is listed as being acidic, and the F^- ion is listed as a base, so we must directly compare the K_a and the K_b of the two ions. K_a of NH_4^+ is 5.6×10^{-10} , which seems very small, yet the K_b of F^- is 1.4×10^{-11} , so the solution is acidic, since $K_a > K_b$.

Check Your Learning

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

- (a) K_2CO_3
- (b) CaCl_2
- (c) KH_2PO_4
- (d) $(\text{NH}_4)_2\text{CO}_3$
- (e) AlBr_3

Note:

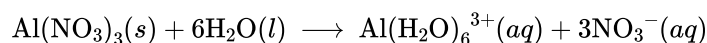
Answer:

(a) basic; (b) neutral; (c) acidic; (d) basic; (e) acidic

The Ionization of Hydrated Metal Ions

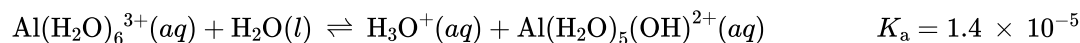
If we measure the pH of the solutions of a variety of metal ions we will find that these ions act as weak acids when in solution. The aluminum ion is an example. When aluminum nitrate dissolves in water, the aluminum ion reacts with water to give a hydrated aluminum ion, $\text{Al}(\text{H}_2\text{O})_6^{3+}$, dissolved in bulk water. What this means is that the aluminum ion has the strongest interactions with the six closest water molecules (the so-called first solvation shell), even though it does interact with the other water molecules surrounding this $\text{Al}(\text{H}_2\text{O})_6^{3+}$ cluster as well:

Equation:



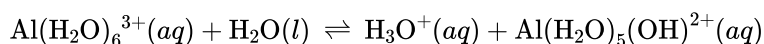
We frequently see the formula of this ion written simply as “ $\text{Al}^{3+}(aq)$ ”, without explicitly noting that six water molecules are covalently bonded to the aluminum ion. This is similar to the simplification of the formula of the hydronium ion, H_3O^+ to H^+ . In this case, a bonded water molecule acts as a weak acid ([link](#)) and donates a proton to a water molecule.

Equation:

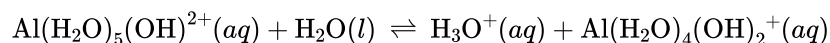


The conjugate base produced by this process contains five other bonded water molecules capable of acting as acids, and so the sequential or step-wise transfer of protons is possible as depicted in the equations below:

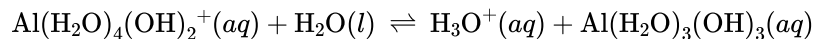
Equation:



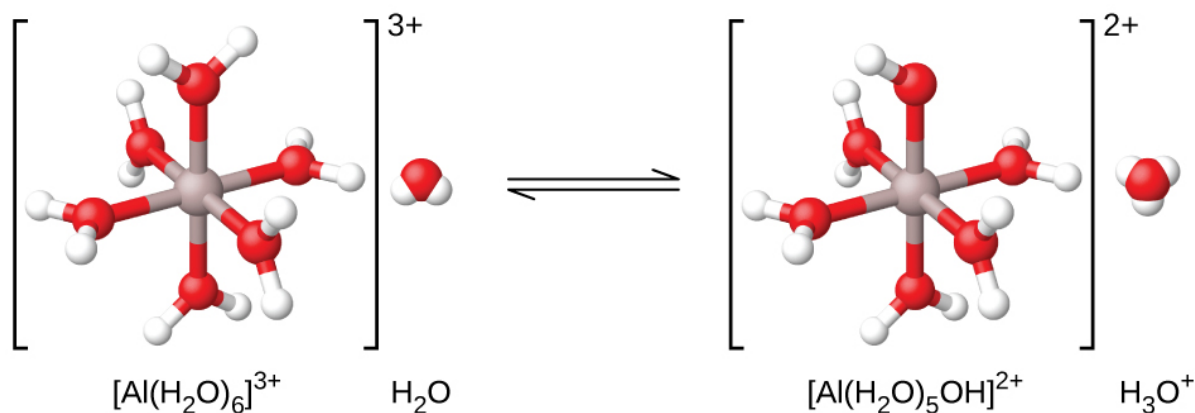
Equation:



Equation:



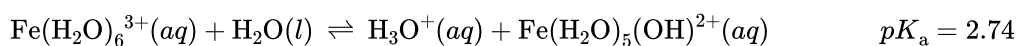
This is an example of a polyprotic acid, the topic of discussion in a later section of this chapter.



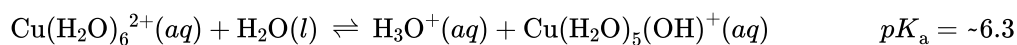
When an aluminum ion reacts with water, the hydrated aluminum ion becomes a weak acid.

Additional examples of the first stage in the ionization of hydrated metal ions are:

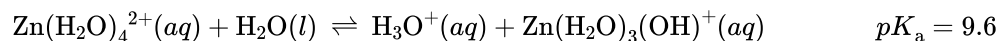
Equation:



Equation:



Equation:



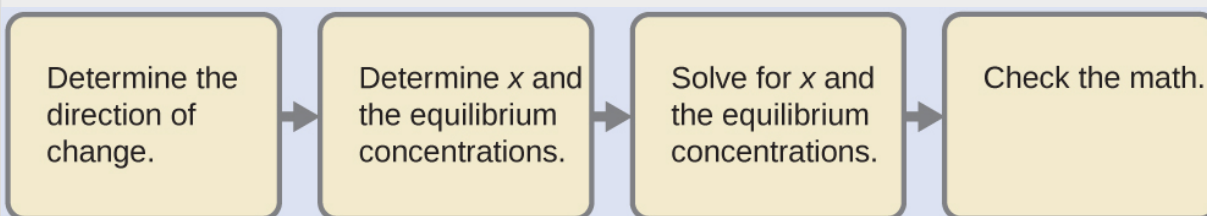
Example:

Hydrolysis of $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$

Calculate the pH of a 0.10-M solution of aluminum chloride, which dissolves completely to give the hydrated aluminum ion $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ in solution.

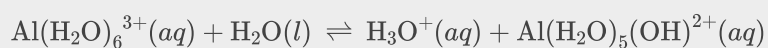
Solution

In spite of the unusual appearance of the acid, this is a typical acid ionization problem.



Determine. The K_{a} are:

the equation
direction for the
of change reaction
and



$K_{\text{a}} = 1.4$

Determine x and

Use the

equilibrium concentrations. table:

	$\text{Al}(\text{H}_2\text{O})_6^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}$		
Initial concentration (M)	0.10	~0	0
Change (M)	-x	x	x
Equilibrium constant (M)	$0.10 - x$	x	x

Solve for x and the equilibrium concentrations for the

. Substituting the expressions for the equilibrium concentrations into the equation for the ionization constant yields:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}]}{[\text{Al}(\text{H}_2\text{O})_6^{3+}]} = \frac{(x)(x)}{0.10 - x} = 1.4 \times 10^{-5}$$

Equation:

Solving this equation gives:

$$x = 1.2 \times 10^{-3}$$

Check the work. The arithmetic checks; when $1.2 \times 10^{-3} M$ is substituted for x , the result $= K_a$.

Check Your Learning

What is $[\text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}]$ in a 0.15-M solution of $\text{Al}(\text{NO}_3)_3$ that contains enough of the strong acid HNO_3 to bring $[\text{H}_3\text{O}^+]$ to 0.10 M?

Note:

Answer:

$$2.1 \times 10^{-5} M$$

The constants for the different stages of ionization are not known for many metal ions, so we cannot calculate the extent of their ionization. However, practically all hydrated metal ions other than those of the alkali metals ionize to give acidic solutions. Ionization increases as the charge of the metal ion increases or as the size of the metal ion decreases.

Key Concepts and Summary

The characteristic properties of aqueous solutions of Brønsted-Lowry acids are due to the presence of hydronium ions; those of aqueous solutions of Brønsted-Lowry bases are due to the presence of hydroxide ions. The neutralization that occurs when aqueous solutions of acids and bases are combined results from the reaction of the hydronium and hydroxide ions to form water. Some salts formed in neutralization reactions may make the product solutions slightly acidic or slightly basic.

Solutions that contain salts or hydrated metal ions have a pH that is determined by the extent of the hydrolysis of the ions in the solution. The pH of the solutions may be calculated using familiar equilibrium techniques, or it may be qualitatively determined to be acidic, basic, or neutral depending on the relative K_a and K_b of the ions involved.

Chemistry End of Chapter Exercises

Exercise:

Problem: Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

(a) $\text{Al}(\text{NO}_3)_3$

(b) RbI

(c) KHCO_2

(d) $\text{CH}_3\text{NH}_3\text{Br}$

Exercise:

Problem: Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

(a) FeCl_3

(b) K_2CO_3

(c) NH_4Br

(d) KClO_4

Solution:

(a) acidic; (b) basic; (c) acidic; (d) neutral

Exercise:

Problem:

Novocaine, $\text{C}_{13}\text{H}_{21}\text{O}_2\text{N}_2\text{Cl}$, is the salt of the base procaine and hydrochloric acid. The ionization constant for procaine is 7×10^{-6} . Is a solution of novocaine acidic or basic? What are $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$, and pH of a 2.0% solution by mass of novocaine, assuming that the density of the solution is 1.0 g/mL.

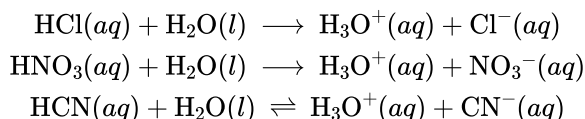
Polyprotic Acids

By the end of this section, you will be able to:

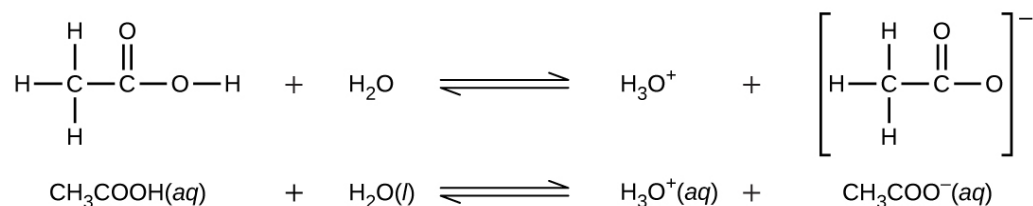
- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton

We can classify acids by the number of protons per molecule that they can give up in a reaction. Acids such as HCl, HNO₃, and HCN that contain one ionizable hydrogen atom in each molecule are called **monoprotic acids**. Their reactions with water are:

Equation:



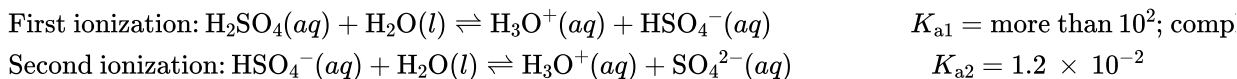
Even though it contains four hydrogen atoms, acetic acid, CH₃CO₂H, is also monoprotic because only the hydrogen atom from the carboxyl group (COOH) reacts with bases:



Similarly, monoprotic bases are bases that will accept a single proton.

Diprotic acids contain two ionizable hydrogen atoms per molecule; ionization of such acids occurs in two steps. The first ionization always takes place to a greater extent than the second ionization. For example, sulfuric acid, a strong acid, ionizes as follows:

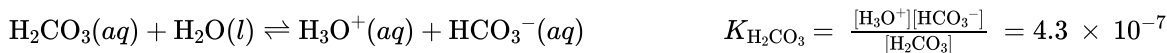
Equation:



This **stepwise ionization** process occurs for all polyprotic acids. When we make a solution of a weak diprotic acid, we get a solution that contains a mixture of acids. Carbonic acid, H₂CO₃, is an example of a weak diprotic acid. The first ionization of carbonic acid yields hydronium ions and bicarbonate ions in small amounts.

Equation:

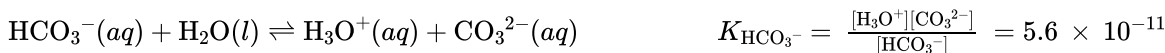
First ionization:



The bicarbonate ion can also act as an acid. It ionizes and forms hydronium ions and carbonate ions in even smaller quantities.

Equation:

Second ionization:



$K_{\text{H}_2\text{CO}_3}$ is larger than $K_{\text{HCO}_3^-}$ by a factor of 10^4 , so H_2CO_3 is the dominant producer of hydronium ion in the solution. This means that little of the HCO_3^- formed by the ionization of H_2CO_3 ionizes to give hydronium ions (and carbonate ions), and the concentrations of H_3O^+ and HCO_3^- are practically equal in a pure aqueous solution of H_2CO_3 .

If the first ionization constant of a weak diprotic acid is larger than the second by a factor of at least 20, it is appropriate to treat the first ionization separately and calculate concentrations resulting from it before calculating concentrations of species resulting from subsequent ionization. This can simplify our work considerably because we can determine the concentration of H_3O^+ and the conjugate base from the first ionization, then determine the concentration of the conjugate base of the second ionization in a solution with concentrations determined by the first ionization.

Example:

Ionization of a Diprotic Acid

When we buy soda water (carbonated water), we are buying a solution of carbon dioxide in water. The solution is acidic because CO_2 reacts with water to form carbonic acid, H_2CO_3 . What are $[\text{H}_3\text{O}^+]$, $[\text{HCO}_3^-]$, and $[\text{CO}_3^{2-}]$ in a saturated solution of CO_2 with an initial $[\text{H}_2\text{CO}_3] = 0.033 \text{ M}$?

Equation:

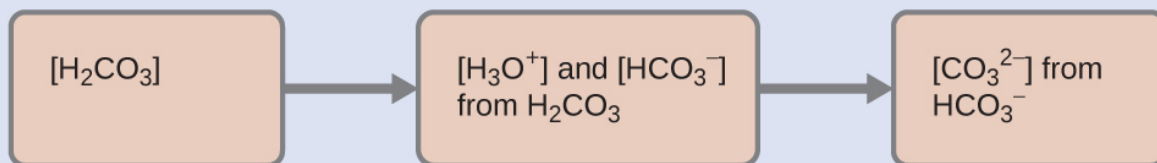


Equation:

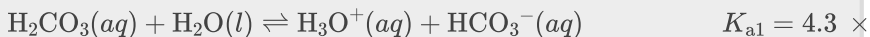


Solution

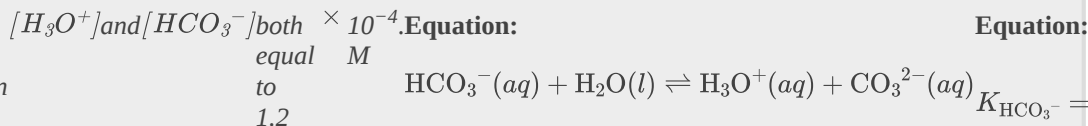
As indicated by the ionization constants, H_2CO_3 is a much stronger acid than HCO_3^- , so H_2CO_3 is the dominant producer of hydronium ion in solution. Thus there are two parts in the solution of this problem: (1) Using the customary four steps, we determine the concentration of H_3O^+ and HCO_3^- produced by ionization of H_2CO_3 . (2) Then we determine the concentration of CO_3^{2-} in a solution with the concentration of H_3O^+ and HCO_3^- determined in (1). To summarize:



Determine the H_3O^+ and HCO_3^- concentrations of



Determine the concentration of CO_3^{2-} in a solution at equilibrium with



To summarize: In part 1 of this example, we found that the H_2CO_3 in a 0.033-M solution ionizes slightly and at equilibrium $[\text{H}_2\text{CO}_3] = 0.033\text{ M}$; $[\text{H}_3\text{O}^+] = 1.2 \times 10^{-4}$; and $[\text{HCO}_3^-] = 1.2 \times 10^{-4}\text{ M}$. In part 2, we determined that $[\text{CO}_3^{2-}] = 5.6 \times 10^{-11}\text{ M}$.

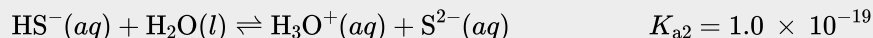
Check Your Learning

The concentration of H_2S in a saturated aqueous solution at room temperature is approximately 0.1 M. Calculate $[\text{H}_3\text{O}^+]$, $[\text{HS}^-]$, and $[\text{S}^{2-}]$ in the solution:

Equation:



Equation:



Note:

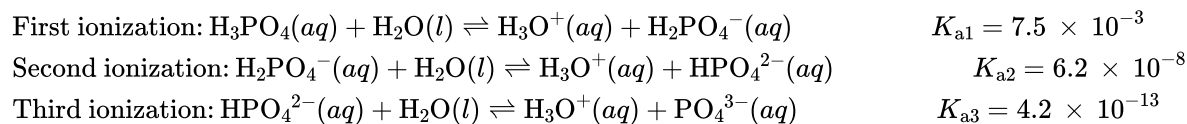
Answer:

$[\text{H}_2\text{S}] = 0.1\text{ M}$; $[\text{H}_3\text{O}^+] = [\text{HS}^-] = 0.000094\text{ M}$; $[\text{S}^{2-}] = 1 \times 10^{-19}\text{ M}$

We note that the concentration of the sulfide ion is the same as K_{a2} . This is due to the fact that each subsequent dissociation occurs to a lesser degree (as acid gets weaker).

A **triprotic acid** is an acid that has three dissociable protons that undergo stepwise ionization: Phosphoric acid is a typical example:

Equation:

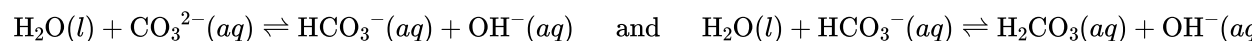


As with the diprotic acids, the differences in the ionization constants of these reactions tell us that in each successive step the degree of ionization is significantly weaker. This is a general characteristic of polyprotic acids and successive ionization constants often differ by a factor of about 10^5 to 10^6 .

This set of three dissociation reactions may appear to make calculations of equilibrium concentrations in a solution of H_3PO_4 complicated. However, because the successive ionization constants differ by a factor of 10^5 to 10^6 , the calculations can be broken down into a series of parts similar to those for diprotic acids.

Polyprotic bases can accept more than one hydrogen ion in solution. The carbonate ion is an example of a **diprotic base**, since it can accept up to two protons. Solutions of alkali metal carbonates are quite alkaline, due to the reactions:

Equation:



Key Concepts and Summary

An acid that contains more than one ionizable proton is a polyprotic acid. The protons of these acids ionize in steps. The differences in the acid ionization constants for the successive ionizations of the protons in a polyprotic acid usually vary by roughly five orders of magnitude. As long as the difference between the successive values of K_a of the acid is greater than about a factor of 20, it is appropriate to break down the calculations of the concentrations of the ions in solution into a series of steps.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Which of the following concentrations would be practically equal in a calculation of the equilibrium concentrations in a 0.134-M solution of H_2CO_3 , a diprotic acid: $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$, $[\text{H}_2\text{CO}_3]$, $[\text{HCO}_3^-]$, $[\text{CO}_3^{2-}]$? No calculations are needed to answer this question.

Solution:

$[\text{H}_3\text{O}^+]$ and $[\text{HCO}_3^-]$ are practically equal

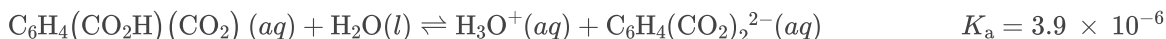
Exercise:

Problem: Calculate the concentration of each species present in a 0.050-M solution of H_2S .

Exercise:

Problem:

Calculate the concentration of each species present in a 0.010-M solution of phthalic acid, $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$.



Solution:

$[\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2] 7.2 \times 10^{-3} \text{ M}$, $[\text{C}_6\text{H}_4(\text{CO}_2\text{H})(\text{CO}_2)^-] = [\text{H}_3\text{O}^+] 2.8 \times 10^{-3} \text{ M}$, $[\text{C}_6\text{H}_4(\text{CO}_2)_2^{2-}] 3.9 \times 10^{-6} \text{ M}$, $[\text{OH}^-] 3.6 \times 10^{-12} \text{ M}$

Exercise:

Problem:

Salicylic acid, $\text{HOC}_6\text{H}_4\text{CO}_2\text{H}$, and its derivatives have been used as pain relievers for a long time. Salicylic acid occurs in small amounts in the leaves, bark, and roots of some vegetation (most notably historically in the bark of the willow tree). Extracts of these plants have been used as medications for centuries. The acid was first isolated in the laboratory in 1838.

(a) Both functional groups of salicylic acid ionize in water, with $K_a = 1.0 \times 10^{-3}$ for the $-\text{CO}_2\text{H}$ group and 4.2×10^{-13} for the $-\text{OH}$ group. What is the pH of a saturated solution of the acid (solubility = 1.8 g/L).

(b) Aspirin was discovered as a result of efforts to produce a derivative of salicylic acid that would not be irritating to the stomach lining. Aspirin is acetylsalicylic acid, $\text{CH}_3\text{CO}_2\text{C}_6\text{H}_4\text{CO}_2\text{H}$. The $-\text{CO}_2\text{H}$ functional group is still present, but its acidity is reduced, $K_a = 3.0 \times 10^{-4}$. What is the pH of a solution of aspirin with the same concentration as a saturated solution of salicylic acid (See Part a).

(c) Under some conditions, aspirin reacts with water and forms a solution of salicylic acid and acetic acid:
 $\text{CH}_3\text{CO}_2\text{C}_6\text{H}_4\text{CO}_2\text{H}(aq) + \text{H}_2\text{O}(l) \longrightarrow \text{HOC}_6\text{H}_4\text{CO}_2\text{H}(aq) + \text{CH}_3\text{CO}_2\text{H}(aq)$

i. Which of the acids, salicylic acid or acetic acid, produces more hydronium ions in such a solution?

- ii. What are the concentrations of molecules and ions in a solution produced by the hydrolysis of 0.50 g of aspirin dissolved in enough water to give 75 mL of solution?

Exercise:

Problem: The ion HTe^- is an amphiprotic species; it can act as either an acid or a base.

- (a) What is K_a for the acid reaction of HTe^- with H_2O ?
- (b) What is K_b for the reaction in which HTe^- functions as a base in water?
- (c) Demonstrate whether or not the second ionization of H_2Te can be neglected in the calculation of $[\text{HTe}^-]$ in a 0.10 M solution of H_2Te .

Solution:

- (a) $K_{a2} = 1.5 \times 10^{-11}$;
- (b) $K_b = 4.3 \times 10^{-12}$;
- (c) $\frac{[\text{Te}^{2-}][\text{H}_3\text{O}^+]}{[\text{HTe}^-]} = \frac{(x)(0.0141+x)}{(0.0141-x)} \approx \frac{(x)(0.0141)}{0.0141} = 1.5 \times 10^{-11}$

Solving for x gives $1.5 \times 10^{-11} \text{ M}$. Therefore, compared with 0.014 M, this value is negligible ($1.1 \times 10^{-7}\%$).

Glossary

diprotic acid

acid containing two ionizable hydrogen atoms per molecule. A diprotic acid ionizes in two steps

diprotic base

base capable of accepting two protons. The protons are accepted in two steps

monoprotic acid

acid containing one ionizable hydrogen atom per molecule

stepwise ionization

process in which an acid is ionized by losing protons sequentially

triprotic acid

acid that contains three ionizable hydrogen atoms per molecule; ionization of triprotic acids occurs in three steps

Buffers

By the end of this section, you will be able to:

- Describe the composition and function of acid–base buffers
- Calculate the pH of a buffer before and after the addition of added acid or base

A mixture of a weak acid and its conjugate base (or a mixture of a weak base and its conjugate acid) is called a buffer solution, or a **buffer**. Buffer solutions resist a change in pH when small amounts of a strong acid or a strong base are added ([link](#)). A solution of acetic acid and sodium acetate ($\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$) is an example of a buffer that consists of a weak acid and its salt. An example of a buffer that consists of a weak base and its salt is a solution of ammonia and ammonium chloride ($\text{NH}_3(\text{aq}) + \text{NH}_4\text{Cl}(\text{aq})$).

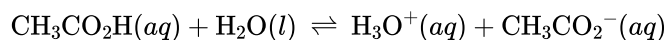


(a) The buffered solution on the left and the unbuffered solution on the right have the same pH (pH 8); they are basic, showing the yellow color of the indicator methyl orange at this pH. (b) After the addition of 1 mL of a 0.01-*M* HCl solution, the buffered solution has not detectably changed its pH but the unbuffered solution has become acidic, as indicated by the change in color of the methyl orange, which turns red at a pH of about 4. (credit: modification of work by Mark Ott)

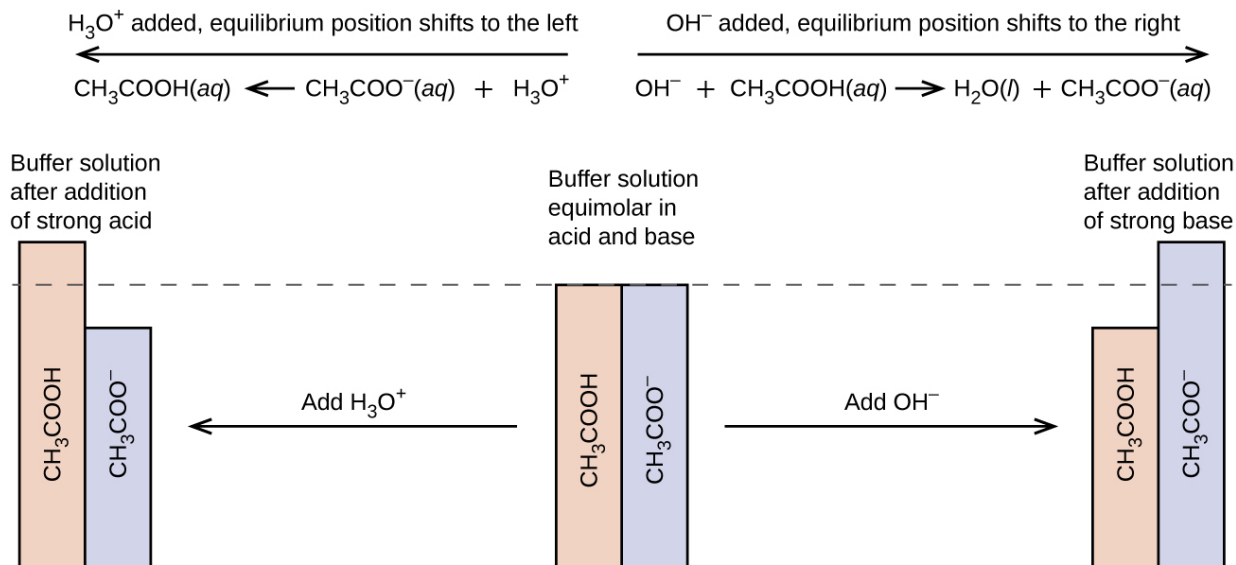
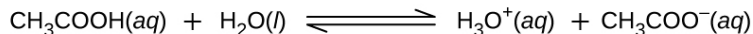
How Buffers Work

A mixture of acetic acid and sodium acetate is acidic because the K_a of acetic acid is greater than the K_b of its conjugate base acetate. It is a buffer because it contains both the weak acid and its salt. Hence, it acts to keep the hydronium ion concentration (and the pH) almost constant by the addition of either a small amount of a strong acid or a strong base. If we add a base such as sodium hydroxide, the hydroxide ions react with the few hydronium ions present. The decrease in hydronium ion concentration causes the acetic acid hydrolysis equilibrium to shift to the right, restoring the hydronium ion concentration almost to its original value, and yielding a relatively modest increase in pH:

Equation:



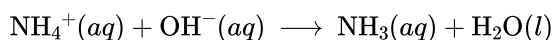
If we add an acid such as hydrochloric acid, the resultant increase in hydronium ion concentration shifts the equilibrium to the left. This effectively converts the added strong acid to a much weaker acid (acetic acid), and the buffer solution thus experiences only a slight decrease in pH.



This diagram shows the buffer action of these reactions.

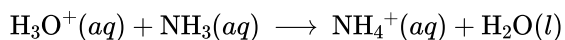
A mixture of ammonia and ammonium chloride is basic because the K_b for ammonia is greater than the K_a for the ammonium ion. It is a buffer because it also contains the salt of the weak base. If we add a base (hydroxide ions), ammonium ions in the buffer react with the hydroxide ions to form ammonia and water and reduce the hydroxide ion concentration almost to its original value:

Equation:



If we add an acid (hydronium ions), ammonia molecules in the buffer mixture react with the hydronium ions to form ammonium ions and reduce the hydronium ion concentration almost to its original value:

Equation:



The three parts of the following example illustrate the change in pH that accompanies the addition of base to a buffered solution of a weak acid and to an unbuffered solution of a strong acid.

Example:

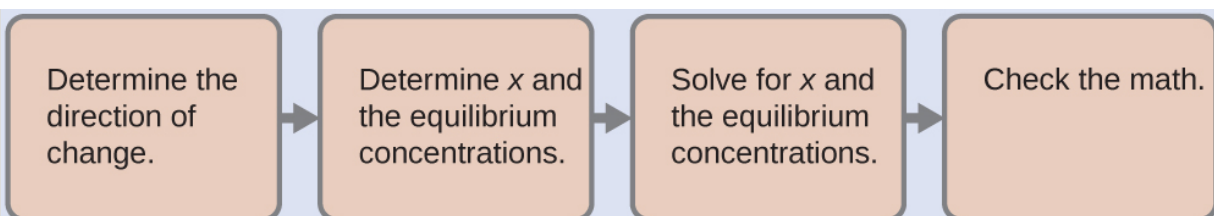
pH Changes in Buffered and Unbuffered Solutions

Acetate buffers are used in biochemical studies of enzymes and other chemical components of cells to prevent pH changes that might change the biochemical activity of these compounds.

(a) Calculate the pH of an acetate buffer that is a mixture with 0.10 M acetic acid and 0.10 M sodium acetate.

Solution

To determine the pH of the buffer solution we use a typical equilibrium calculation (as illustrated in earlier Examples):



Determine the direction of change. The equilibrium mixture of H_3O^+ , CH_3CO_2^- , and $\text{CH}_3\text{CO}_2\text{H}$ is: **Equation:** $\text{CH}_3\text{CO}_2\text{H}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{CO}_2^-(aq)$ The equilibrium constant for C

Determine x and equilibrium concentrations. A table of changes and concentrations follows:

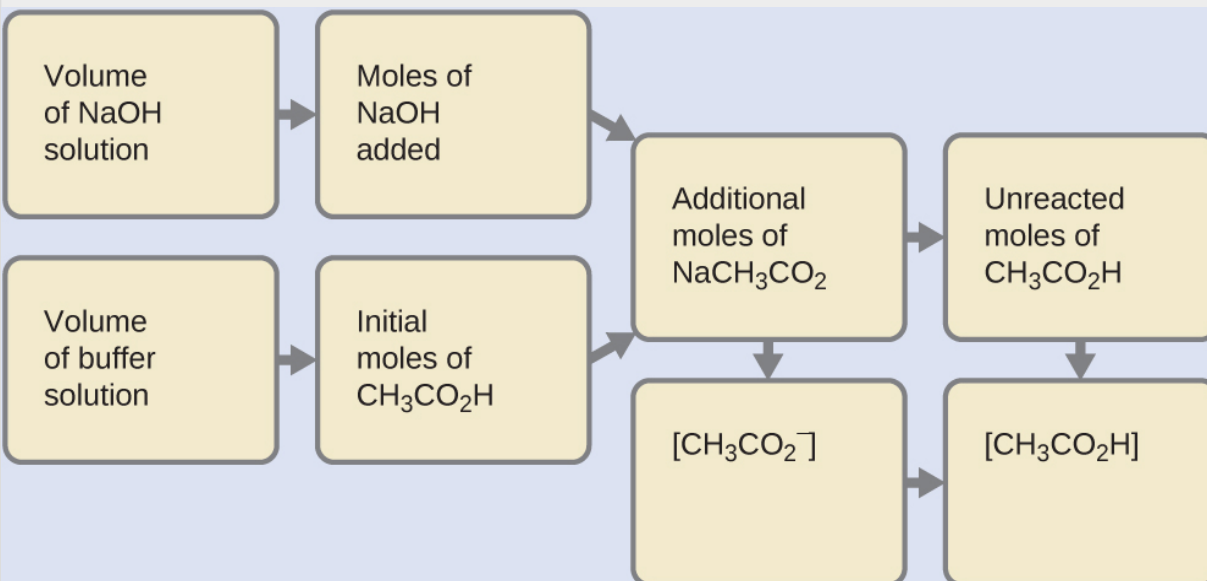
	$\text{CH}_3\text{CO}_2\text{H}$	$+$	H_2O	\rightleftharpoons	H_3O^+	$+$	CH_3CO_2^-
Initial concentration (M)	0.10				~0		0.10
Change (M)	-x				x		x
Equilibrium constant (M)	0.10 - x				x		0.10 + x

Solve for x and the equilibrium concentrations. **Equation:** $x = 1.8 \times 10^{-5} M$ **Equation:** $[\text{H}_3\text{O}^+] = 0 + x = 1.8 \times 10^{-5} M$ **Equation:** $\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log$

Check the work. If we calculate all calculated equilibrium concentrations, we find that the equilibrium value of $Q = K_a$, the reaction coefficient,

(b) Calculate the pH after 1.0 mL of 0.10 M NaOH is added to 100 mL of this buffer, giving a solution with a volume of 101 mL.

First, we calculate the concentrations of an intermediate mixture resulting from the complete reaction between the acid in the buffer and the added base. Then we determine the concentrations of the mixture at the new equilibrium:



Determine the One milliliter M NaOH **Equation:**

moles of NaOH. (0.0010 L) of 0.10 contains: $0.0010 \text{ L} \times \left(\frac{0.10 \text{ mol NaOH}}{1 \text{ L}} \right) = 1.0 \times 10^{-4} \text{ mol NaOH}$

Determine the Before reaction, 0.100 **Equation:**

moles of L of the buffer solution
 $\text{CH}_3\text{CO}_2\text{H}$ contains: $0.100 \text{ L} \times \left(\frac{0.100 \text{ mol CH}_3\text{CO}_2\text{H}}{1 \text{ L}} \right) = 1.00 \times 10^{-2} \text{ mol CH}_3\text{CO}_2\text{H}$

Solve for The $\times 10^{-4}$ mol of $\times 10^{-4}$ mol $\text{CH}_3\text{CO}_2\text{H}$, **Equation:**
the amount 1.0 NaOH of leaving:
of neutralizes CH $(1.0 \times 10^{-2}) - (0.01 \times 10^{-2}) = 0.99 \times 10^{-2} \text{ mol CH}_3\text{CO}_2\text{H}$
 NaCH_3CO_2 1.0
produced.

Find the After $\text{CH}_3\text{CO}_2\text{H}$ and CH_3CO_2^- are **Equation:** **Equation:**
molarity reaction, NaCH_3CO_2 contained in
of the CH 101 mL of $[\text{CH}_3\text{CO}_2\text{H}] = \frac{9.9 \times 10^{-3} \text{ mol}}{0.101 \text{ L}} = 0.098 \text{ M} [\text{NaCH}_3\text{CO}_2] = .$
products. the intermediate solution, so:

(c) For comparison, calculate the pH after 1.0 mL of 0.10 M NaOH is added to 100 mL of a solution of an unbuffered solution with a pH of 4.74 (a $1.8 \times 10^{-5}\text{-M}$ solution of HCl). The volume of the final solution is 101 mL.

Solution

This $1.8 \times 10^{-5}\text{-M}$ solution of HCl has the same hydronium ion concentration as the 0.10-M solution of acetic acid-sodium acetate buffer described in part (a) of this example. The solution contains:

Equation:

$$0.100 \text{ L} \times \left(\frac{1.8 \times 10^{-5} \text{ mol HCl}}{1 \text{ L}} \right) = 1.8 \times 10^{-6} \text{ mol HCl}$$

As shown in part (b), 1 mL of 0.10 M NaOH contains 1.0×10^{-4} mol of NaOH. When the NaOH and HCl solutions are mixed, the HCl is the limiting reagent in the reaction. All of the HCl reacts, and the amount of NaOH that remains is:

Equation:

$$(1.0 \times 10^{-4}) - (1.8 \times 10^{-6}) = 9.8 \times 10^{-5} \text{ M}$$

The concentration of NaOH is:

Equation:

$$\frac{9.8 \times 10^{-5} \text{ M NaOH}}{0.101 \text{ L}} = 9.7 \times 10^{-4} \text{ M}$$

The pOH of this solution is:

Equation:

$$\text{pOH} = -\log [\text{OH}^-] = -\log (9.7 \times 10^{-4}) = 3.01$$

The pH is:

Equation:

$$\text{pH} = 14.00 - \text{pOH} = 10.99$$

The pH changes from 4.74 to 10.99 in this unbuffered solution. This compares to the change of 4.74 to 4.75 that occurred when the same amount of NaOH was added to the buffered solution described in part (b).

Check Your Learning

Show that adding 1.0 mL of 0.10 M HCl changes the pH of 100 mL of a 1.8×10^{-5} M HCl solution from 4.74 to 3.00.

Note:**Answer:**

Initial pH of 1.8×10^{-5} M HCl; $\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log[1.8 \times 10^{-5}] = 4.74$

Moles of H_3O^+ in 100 mL 1.8×10^{-5} M HCl; $1.8 \times 10^{-5} \text{ moles/L} \times 0.100 \text{ L} = 1.8 \times 10^{-6}$

Moles of H_3O^+ added by addition of 1.0 mL of 0.10 M HCl: $0.10 \text{ moles/L} \times 0.0010 \text{ L} = 1.0 \times 10^{-4} \text{ moles}$; final pH after addition of 1.0 mL of 0.10 M HCl:

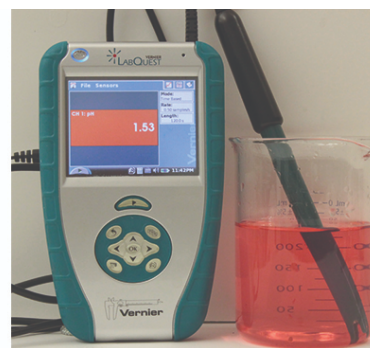
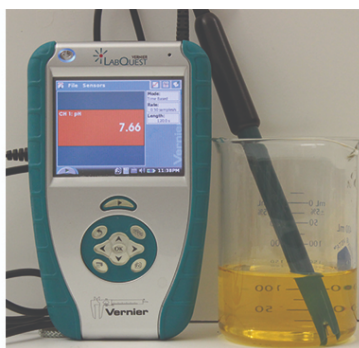
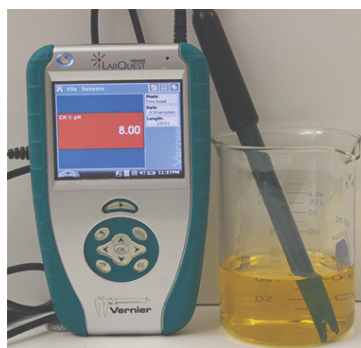
Equation:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log\left(\frac{\text{total moles } \text{H}_3\text{O}^+}{\text{total volume}}\right) = -\log\left(\frac{1.0 \times 10^{-4} \text{ mol} + 1.8 \times 10^{-6} \text{ mol}}{101 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)}\right) = 3.00$$

If we add an acid or a base to a buffer that is a mixture of a weak base and its salt, the calculations of the changes in pH are analogous to those for a buffer mixture of a weak acid and its salt.

Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant ([link](#)). If we add so much base to a buffer that the weak acid is exhausted, no more buffering action toward the base is possible. On the other hand, if we add an excess of acid, the weak base would be exhausted, and no more buffering action toward any additional acid would be possible. In fact, we do not even need to exhaust all of the acid or base in a buffer to overwhelm it; its buffering action will diminish rapidly as a given component nears depletion.



The indicator color (methyl orange) shows that a small amount of acid added to a buffered solution of pH 8 (beaker on the left) has little effect on the buffered system (middle beaker). However, a large amount of acid

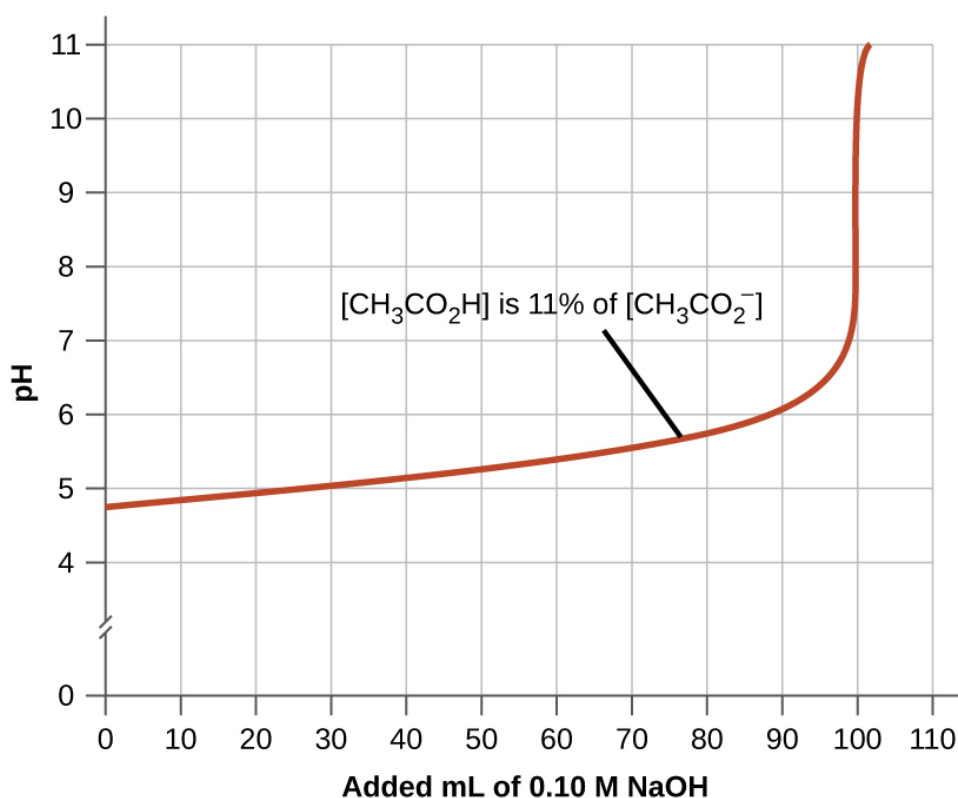
exhausts the buffering capacity of the solution and the pH changes dramatically (beaker on the right). (credit: modification of work by Mark Ott)

The **buffer capacity** is the amount of acid or base that can be added to a given volume of a buffer solution before the pH changes significantly, usually by one unit. Buffer capacity depends on the amounts of the weak acid and its conjugate base that are in a buffer mixture. For example, 1 L of a solution that is 1.0 M in acetic acid and 1.0 M in sodium acetate has a greater buffer capacity than 1 L of a solution that is 0.10 M in acetic acid and 0.10 M in sodium acetate even though both solutions have the same pH. The first solution has more buffer capacity because it contains more acetic acid and acetate ion.

Selection of Suitable Buffer Mixtures

There are two useful rules of thumb for selecting buffer mixtures:

1. A good buffer mixture should have about equal concentrations of both of its components. A buffer solution has generally lost its usefulness when one component of the buffer pair is less than about 10% of the other. [\[link\]](#) shows an acetic acid-acetate ion buffer as base is added. The initial pH is 4.74. A change of 1 pH unit occurs when the acetic acid concentration is reduced to 11% of the acetate ion concentration.

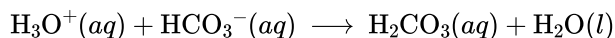


The graph, an illustration of buffering action, shows change of pH as an increasing amount of a 0.10-M NaOH solution is added to 100 mL of a buffer solution in which, initially, $[\text{CH}_3\text{CO}_2\text{H}] = 0.10\text{ M}$ and $[\text{CH}_3\text{CO}_2^-] = 0.10\text{ M}$.

2. Weak acids and their salts are better as buffers for pHs less than 7; weak bases and their salts are better as buffers for pHs greater than 7.

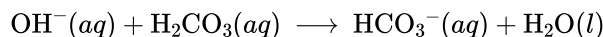
Blood is an important example of a buffered solution, with the principal acid and ion responsible for the buffering action being carbonic acid, H_2CO_3 , and the bicarbonate ion, HCO_3^- . When a hydronium ion is introduced to the blood stream, it is removed primarily by the reaction:

Equation:



An added hydroxide ion is removed by the reaction:

Equation:



The added strong acid or base is thus effectively converted to the much weaker acid or base of the buffer pair (H_3O^+ is converted to H_2CO_3 and OH^- is converted to HCO_3^-). The pH of human blood thus remains very near the value determined by the buffer pairs pK_a , in this case, 7.35. Normal variations in blood pH are usually less than 0.1, and pH changes of 0.4 or greater are likely to be fatal.

The Henderson-Hasselbalch Equation

The ionization-constant expression for a solution of a weak acid can be written as:

Equation:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

Rearranging to solve for $[\text{H}_3\text{O}^+]$, we get:

Equation:

$$[\text{H}_3\text{O}^+] = K_a \times \frac{[\text{HA}]}{[\text{A}^-]}$$

Taking the negative logarithm of both sides of this equation, we arrive at:

Equation:

$$-\log[\text{H}_3\text{O}^+] = -\log K_a - \log \frac{[\text{HA}]}{[\text{A}^-]},$$

which can be written as

Equation:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

where pK_a is the negative of the common logarithm of the ionization constant of the weak acid ($\text{pK}_a = -\log K_a$). This equation relates the pH, the ionization constant of a weak acid, and the concentrations of the weak acid and its salt in a buffered solution. Scientists often use this expression, called the **Henderson-Hasselbalch equation**, to calculate the pH of buffer solutions. It is important to note that the “x is small” assumption must be valid to use this equation.

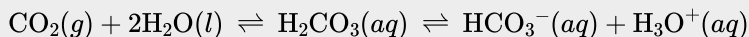
Note:**Lawrence Joseph Henderson and Karl Albert Hasselbalch**

Lawrence Joseph Henderson (1878–1942) was an American physician, biochemist and physiologist, to name only a few of his many pursuits. He obtained a medical degree from Harvard and then spent 2 years studying in Strasbourg, then a part of Germany, before returning to take a lecturer position at Harvard. He eventually became a professor at Harvard and worked there his entire life. He discovered that the acid-base balance in human blood is regulated by a buffer system formed by the dissolved carbon dioxide in blood. He wrote an equation in 1908 to describe the carbonic acid-carbonate buffer system in blood. Henderson was broadly knowledgeable; in addition to his important research on the physiology of blood, he also wrote on the adaptations of organisms and their fit with their environments, on sociology and on university education. He also founded the Fatigue Laboratory, at the Harvard Business School, which examined human physiology with specific focus on work in industry, exercise, and nutrition.

In 1916, Karl Albert Hasselbalch (1874–1962), a Danish physician and chemist, shared authorship in a paper with Christian Bohr in 1904 that described the Bohr effect, which showed that the ability of hemoglobin in the blood to bind with oxygen was inversely related to the acidity of the blood and the concentration of carbon dioxide. The pH scale was introduced in 1909 by another Dane, Sørensen, and in 1912, Hasselbalch published measurements of the pH of blood. In 1916, Hasselbalch expressed Henderson's equation in logarithmic terms, consistent with the logarithmic scale of pH, and thus the Henderson-Hasselbalch equation was born.

Note:**Medicine: The Buffer System in Blood**

The normal pH of human blood is about 7.4. The carbonate buffer system in the blood uses the following equilibrium reaction:

Equation:

The concentration of carbonic acid, H_2CO_3 is approximately 0.0012 M, and the concentration of the hydrogen carbonate ion, HCO_3^- , is around 0.024 M. Using the Henderson-Hasselbalch equation and the $\text{p}K_a$ of carbonic acid at body temperature, we can calculate the pH of blood:

Equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} = 6.4 + \log \frac{0.024}{0.0012} = 7.7$$

The fact that the H_2CO_3 concentration is significantly lower than that of the HCO_3^- ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.

Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the HCO_3^- ion, producing H_2CO_3 . An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes CO_2 from the blood through the lungs driving the equilibrium reaction such that $[\text{H}_3\text{O}^+]$ is lowered. If the blood is too alkaline, a lower breath rate increases CO_2 concentration in the blood, driving the equilibrium reaction the other way, increasing $[\text{H}^+]$ and restoring an appropriate pH.

Note:



View [information](#) on the buffer system encountered in natural waters.

Key Concepts and Summary

A solution containing a mixture of a weak acid and its conjugate base, or of a weak base and its conjugate acid, is called a buffer solution. The presence of a weak conjugate acid-base pair provides reactants that may neutralize small additions of strong acid or base, yielding weaker conjugate partners. The hydronium ion concentration of a buffer solution therefore does not change significantly when a small amount of acid or base is added.

Key Equations

- $pK_a = -\log K_a$
- $pK_b = -\log K_b$
- $pH = pK_a + \log \frac{[A^-]}{[HA]}$

Exercise:

Problem:

Explain why a buffer can be prepared from a mixture of NH_4Cl and $NaOH$ but not from NH_3 and $NaOH$.

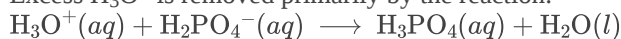
Exercise:

Problem:

Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the acid H_3PO_4 and a salt of its conjugate base NaH_2PO_4 .

Solution:

Excess H_3O^+ is removed primarily by the reaction:



Excess base is removed by the reaction:



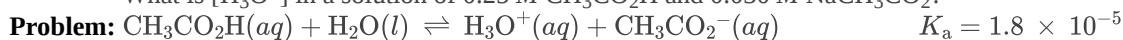
Exercise:

Problem:

Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the base NH_3 and a salt of its conjugate acid NH_4Cl .

Exercise:

What is $[H_3O^+]$ in a solution of 0.25 M CH_3CO_2H and 0.030 M $NaCH_3CO_2$?

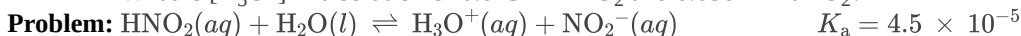


Solution:

$$[H_3O^+] = 1.5 \times 10^{-4} M$$

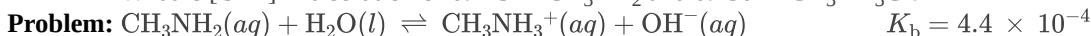
Exercise:

What is $[\text{H}_3\text{O}^+]$ in a solution of 0.075 M HNO_2 and 0.030 M NaNO_2 ?



Exercise:

What is $[\text{OH}^-]$ in a solution of 0.125 M CH_3NH_2 and 0.130 M $\text{CH}_3\text{NH}_3\text{Cl}$?

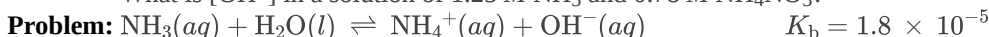


Solution:

$$[\text{OH}^-] = 4.2 \times 10^{-4} \text{ M}$$

Exercise:

What is $[\text{OH}^-]$ in a solution of 1.25 M NH_3 and 0.78 M NH_4NO_3 ?



Exercise:

Problem:

What concentration of NH_4NO_3 is required to make $[\text{OH}^-] = 1.0 \times 10^{-5}$ in a 0.200-M solution of NH_3 ?

Solution:

$$[\text{NH}_4\text{NO}_3] = 0.36 \text{ M}$$

Exercise:

Problem: What concentration of NaF is required to make $[\text{H}_3\text{O}^+] = 2.3 \times 10^{-4}$ in a 0.300-M solution of HF?

Exercise:

Problem:

What is the effect on the concentration of acetic acid, hydronium ion, and acetate ion when the following are added to an acidic buffer solution of equal concentrations of acetic acid and sodium acetate:

- (a) HCl
 - (b) KCH_3CO_2
 - (c) NaCl
 - (d) KOH
 - (e) $\text{CH}_3\text{CO}_2\text{H}$
-

Solution:

- (a) The added HCl will increase the concentration of H_3O^+ slightly, which will react with CH_3CO_2^- and produce $\text{CH}_3\text{CO}_2\text{H}$ in the process. Thus, $[\text{CH}_3\text{CO}_2^-]$ decreases and $[\text{CH}_3\text{CO}_2\text{H}]$ increases.
- (b) The added KCH_3CO_2 will increase the concentration of $[\text{CH}_3\text{CO}_2^-]$ which will react with H_3O^+ and produce $\text{CH}_3\text{CO}_2\text{H}$ in the process. Thus, $[\text{H}_3\text{O}^+]$ decreases slightly and $[\text{CH}_3\text{CO}_2\text{H}]$ increases.
- (c) The added NaCl will have no effect on the concentration of the ions.
- (d) The added KOH will produce OH^- ions, which will react with the H_3O^+ , thus reducing $[\text{H}_3\text{O}^+]$. Some additional $\text{CH}_3\text{CO}_2\text{H}$ will dissociate, producing $[\text{CH}_3\text{CO}_2^-]$ ions in the process. Thus, $[\text{CH}_3\text{CO}_2\text{H}]$ decreases

slightly and $[\text{CH}_3\text{CO}_2^-]$ increases.

(e) The added $\text{CH}_3\text{CO}_2\text{H}$ will increase its concentration, causing more of it to dissociate and producing more $[\text{CH}_3\text{CO}_2^-]$ and H_3O^+ in the process. Thus, $[\text{H}_3\text{O}^+]$ increases slightly and $[\text{CH}_3\text{CO}_2^-]$ increases.

Exercise:

Problem:

What is the effect on the concentration of ammonia, hydroxide ion, and ammonium ion when the following are added to a basic buffer solution of equal concentrations of ammonia and ammonium nitrate:

- (a) KI
- (b) NH_3
- (c) HI
- (d) NaOH
- (e) NH_4Cl

Exercise:

Problem:

What will be the pH of a buffer solution prepared from 0.20 mol NH_3 , 0.40 mol NH_4NO_3 , and just enough water to give 1.00 L of solution?

Solution:

pH = 8.95

Exercise:

Problem:

Calculate the pH of a buffer solution prepared from 0.155 mol of phosphoric acid, 0.250 mole of KH_2PO_4 , and enough water to make 0.500 L of solution.

Exercise:

Problem:

How much solid $\text{NaCH}_3\text{CO}_2 \cdot 3\text{H}_2\text{O}$ must be added to 0.300 L of a 0.50-*M* acetic acid solution to give a buffer with a pH of 5.00? (Hint: Assume a negligible change in volume as the solid is added.)

Solution:

37 g (0.27 mol)

Exercise:

Problem:

What mass of NH_4Cl must be added to 0.750 L of a 0.100-*M* solution of NH_3 to give a buffer solution with a pH of 9.26? (Hint: Assume a negligible change in volume as the solid is added.)

Exercise:

Problem:

A buffer solution is prepared from equal volumes of 0.200 *M* acetic acid and 0.600 *M* sodium acetate. Use 1.80×10^{-5} as K_a for acetic acid.

- (a) What is the pH of the solution?
- (b) Is the solution acidic or basic?
- (c) What is the pH of a solution that results when 3.00 mL of 0.034 M HCl is added to 0.200 L of the original buffer?
-

Solution:

- (a) pH = 5.222;
- (b) The solution is acidic.
- (c) pH = 5.221

Exercise:

Problem: A 5.36-g sample of NH_4Cl was added to 25.0 mL of 1.00 M NaOH and the resulting solution diluted to 0.100 L.

- (a) What is the pH of this buffer solution?
- (b) Is the solution acidic or basic?
- (c) What is the pH of a solution that results when 3.00 mL of 0.034 M HCl is added to the solution?

Exercise:

Problem:

Which acid in [\[link\]](#) is most appropriate for preparation of a buffer solution with a pH of 3.1? Explain your choice.

Solution:

To prepare the best buffer for a weak acid HA and its salt, the ratio $\frac{[\text{H}_3\text{O}^+]}{K_a}$ should be as close to 1 as possible for effective buffer action. The $[\text{H}_3\text{O}^+]$ concentration in a buffer of pH 3.1 is $[\text{H}_3\text{O}^+] = 10^{-3.1} = 7.94 \times 10^{-4} \text{ M}$. We can now solve for K_a of the best acid as follows:

$$\frac{[\text{H}_3\text{O}^+]}{K_a} = 1$$
$$K_a = \frac{[\text{H}_3\text{O}^+]}{1} = 7.94 \times 10^{-4}$$

In [\[link\]](#), the acid with the closest K_a to 7.94×10^{-4} is HF, with a K_a of 7.2×10^{-4} .

Exercise:

Problem:

Which acid in [\[link\]](#) is most appropriate for preparation of a buffer solution with a pH of 3.7? Explain your choice.

Exercise:

Problem:

Which base in [\[link\]](#) is most appropriate for preparation of a buffer solution with a pH of 10.65? Explain your choice.

Solution:

For buffers with pHs > 7, you should use a weak base and its salt. The most effective buffer will have a ratio $\frac{[\text{OH}^-]}{K_b}$ that is as close to 1 as possible. The pOH of the buffer is $14.00 - 10.65 = 3.35$. Therefore, $[\text{OH}^-]$ is $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-3.35} = 4.467 \times 10^{-4} \text{ M}$.

We can now solve for K_b of the best base as follows:

$$\frac{[\text{OH}^-]}{K_b} = 1$$

$$K_b = [\text{OH}^-] = 4.47 \times 10^{-4}$$

In [\[link\]](#), the base with the closest K_b to 4.47×10^{-4} is CH_3NH_2 , with a $K_b = 4.4 \times 10^{-4}$.

Exercise:

Problem:

Which base in [\[link\]](#) is most appropriate for preparation of a buffer solution with a pH of 9.20? Explain your choice.

Exercise:

Problem:

Saccharin, $\text{C}_7\text{H}_4\text{NSO}_3\text{H}$, is a weak acid ($K_a = 2.1 \times 10^{-2}$). If 0.250 L of diet cola with a buffered pH of 5.48 was prepared from $2.00 \times 10^{-3} \text{ g}$ of sodium saccharide, $\text{Na}(\text{C}_7\text{H}_4\text{NSO}_3)$, what are the final concentrations of saccharine and sodium saccharide in the solution?

Solution:

The molar mass of sodium saccharide is 205.169 g/mol. Using the abbreviations HA for saccharin and NaA for sodium saccharide the number of moles of NaA in the solution is:

$$9.75 \times 10^{-6} \text{ mol}$$

The pKa for [HA] is 1.68, so $[\text{HA}] = 6.2 \times 10^{-9} \text{ M}$. Thus, $[\text{A}^-]$ (saccharin ions) is $3.90 \times 10^{-5} \text{ M}$.

Thus, $[\text{A}^-]$ (saccharin ions) is $3.90 \times 10^{-5} \text{ M}$

Exercise:

Problem:

What is the pH of 1.000 L of a solution of 100.0 g of glutamic acid ($\text{C}_5\text{H}_9\text{NO}_4$, a diprotic acid; $K_1 = 8.5 \times 10^{-5}$, $K_2 = 3.39 \times 10^{-10}$) to which has been added 20.0 g of NaOH during the preparation of monosodium glutamate, the flavoring agent? What is the pH when exactly 1 mol of NaOH per mole of acid has been added?

Glossary

buffer capacity

amount of an acid or base that can be added to a volume of a buffer solution before its pH changes significantly (usually by one pH unit)

buffer

mixture of a weak acid or a weak base and the salt of its conjugate; the pH of a buffer resists change when small amounts of acid or base are added

Henderson-Hasselbalch equation

equation used to calculate the pH of buffer solutions

Acid-Base Titrations

By the end of this section, you will be able to:

- Interpret titration curves for strong and weak acid-base systems
- Compute sample pH at important stages of a titration
- Explain the function of acid-base indicators

As seen in the chapter on the stoichiometry of chemical reactions, titrations can be used to quantitatively analyze solutions for their acid or base concentrations. In this section, we will explore the changes in the concentrations of the acidic and basic species present in a solution during the process of a titration.

Titration Curve

Previously, when we studied acid-base reactions in solution, we focused only on the point at which the acid and base were stoichiometrically equivalent. No consideration was given to the pH of the solution before, during, or after the neutralization.

Example:

Calculating pH for Titration Solutions: Strong Acid/Strong Base

A titration is carried out for 25.00 mL of 0.100 M HCl (strong acid) with 0.100 M of a strong base NaOH the titration curve is shown in [\[link\]](#). Calculate the pH at these volumes of added base solution:

- (a) 0.00 mL
- (b) 12.50 mL
- (c) 25.00 mL
- (d) 37.50 mL

Solution

Since HCl is a strong acid, we can assume that all of it dissociates. The initial concentration of H_3O^+ is $[\text{H}_3\text{O}^+]_0 = 0.100 \text{ M}$. When the base solution is added, it also dissociates completely, providing OH^- ions. The H_3O^+ and OH^- ions neutralize each other, so only those of the two that were in excess remain, and their concentration determines the pH. Thus, the solution is initially acidic ($\text{pH} < 7$), but eventually all the hydronium ions present from the original acid are neutralized, and the solution becomes neutral. As more base is added, the solution turns basic. The total initial amount of the hydronium ions is:

Equation:

$$n(\text{H}^+)_0 = [\text{H}_3\text{O}^+]_0 \times 0.02500 \text{ L} = 0.002500 \text{ mol}$$

Once X mL of the 0.100-M base solution is added, the number of moles of the OH^- ions introduced is:

Equation:

$$n(\text{OH}^-)_0 = 0.100 \text{ M} \times X \text{ mL} \times \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right)$$

The total volume becomes: $V = (25.00 \text{ mL} + X \text{ mL}) \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right)$

The number of moles of H_3O^+ becomes:

Equation:

$$n(\text{H}^+) = n(\text{H}^+)_0 - n(\text{OH}^-)_0 = 0.002500 \text{ mol} - 0.100 \text{ M} \times X \text{ mL} \times \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right)$$

The concentration of H_3O^+ is:

Equation:

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \frac{n(\text{H}^+)}{V} = \frac{0.002500 \text{ mol} - 0.100 \text{ M} \times X \text{ mL} \times \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right)}{(25.00 \text{ mL} + X \text{ mL}) \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right)} \\ &= \frac{0.002500 \text{ mol} \times \left(\frac{1000 \text{ mL}}{1 \text{ L}} \right) - 0.100 \text{ M} \times X \text{ mL}}{25.00 \text{ mL} + X \text{ mL}} \end{aligned}$$

Equation:

$$\text{pH} = -\log([\text{H}_3\text{O}^+])$$

The preceding calculations work if $n(\text{H}^+)_0 - n(\text{OH}^-)_0 > 0$ and so $n(\text{H}^+) > 0$. When $n(\text{H}^+)_0 = n(\text{OH}^-)_0$, the H_3O^+ ions from the acid and the OH^- ions from the base mutually neutralize. At this point, the only hydronium ions left are those from the autoionization of water, and there are no OH^- particles to neutralize them. Therefore, in this case:

Equation:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-], [\text{H}_3\text{O}^+] = K_w = 1.0 \times 10^{-14}; [\text{H}_3\text{O}^+] = 1.0 \times 10^{-7}$$

Equation:

$$\text{pH} = -\log(1.0 \times 10^{-7}) = 7.00$$

Finally, when $n(\text{OH}^-)_0 > n(\text{H}^+)_0$, there are not enough H_3O^+ ions to neutralize all the OH^- ions, and instead of $n(\text{H}^+) = n(\text{H}^+)_0 - n(\text{OH}^-)_0$, we calculate:

$$n(\text{OH}^-) = n(\text{OH}^-)_0 - n(\text{H}^+)_0$$

In this case:

Equation:

$$\begin{aligned} [\text{OH}^-] &= \frac{n(\text{OH}^-)}{V} = \frac{0.100 \text{ M} \times X \text{ mL} \times \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) - 0.002500 \text{ mol}}{(25.00 \text{ mL} + X \text{ mL}) \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right)} \\ &= \frac{0.100 \text{ M} \times X \text{ mL} - 0.002500 \text{ mol} \times \left(\frac{1000 \text{ mL}}{1 \text{ L}} \right)}{25.00 \text{ mL} + X \text{ mL}} \end{aligned}$$

Equation:

$$\text{pH} = 14 - \text{pOH} = 14 + \log([\text{OH}^-])$$

Let us now consider the four specific cases presented in this problem:

(a) X = 0 mL

Equation:

$$[\text{H}_3\text{O}^+] = \frac{n(\text{H}^+)}{V} = \frac{0.002500 \text{ mol} \times \left(\frac{1000 \text{ mL}}{1 \text{ L}} \right)}{25.00 \text{ mL}} = 0.1 \text{ M}$$

$$\text{pH} = -\log(0.100) = 1.000$$

(b) X = 12.50 mL

Equation:

$$[\text{H}_3\text{O}^+] = \frac{n(\text{H}^+)}{V} = \frac{0.002500 \text{ mol} \times \left(\frac{1000 \text{ mL}}{1 \text{ L}} \right) - 0.100 \text{ M} \times 12.50 \text{ mL}}{25.00 \text{ mL} + 12.50 \text{ mL}} = 0.0333 \text{ M}$$

$$\text{pH} = -\log(0.0333) = 1.477$$

(c) X = 25.00 mL

Since the volumes and concentrations of the acid and base solutions are the same:

$n(\text{H}^+)_0 = n(\text{OH}^-)_0$, and $\text{pH} = 7.000$, as described earlier.

(d) X = 37.50 mL

In this case:

Equation:

$$n(\text{OH}^-)_0 > n(\text{H}^+)_0$$

Equation:

$$[\text{OH}^-] = \frac{n(\text{OH}^-)}{V} = \frac{0.100 \text{ M} \times 37.50 \text{ mL} - 0.002500 \text{ mol} \times \left(\frac{1000 \text{ mL}}{1 \text{ L}} \right)}{25.00 \text{ mL} + 37.50 \text{ mL}} = 0.0200 \text{ M}$$

$$\text{pH} = 14 - \text{pOH} = 14 + \log([\text{OH}^-]) = 14 + \log(0.0200) = 12.30$$

Check Your Learning

Calculate the pH for the strong acid/strong base titration between 50.0 mL of 0.100 M $\text{HNO}_3(aq)$ and 0.200 M NaOH (titrant) at the listed volumes of added base: 0.00 mL, 15.0 mL, 25.0 mL, and 40.0 mL.

Note:

Answer:

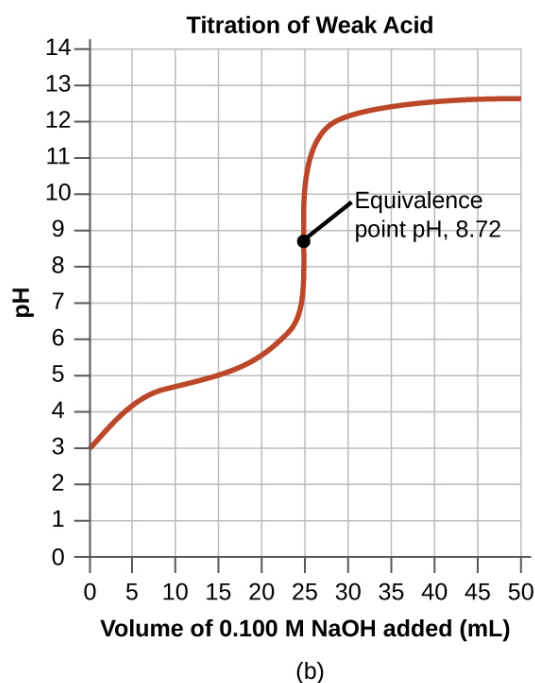
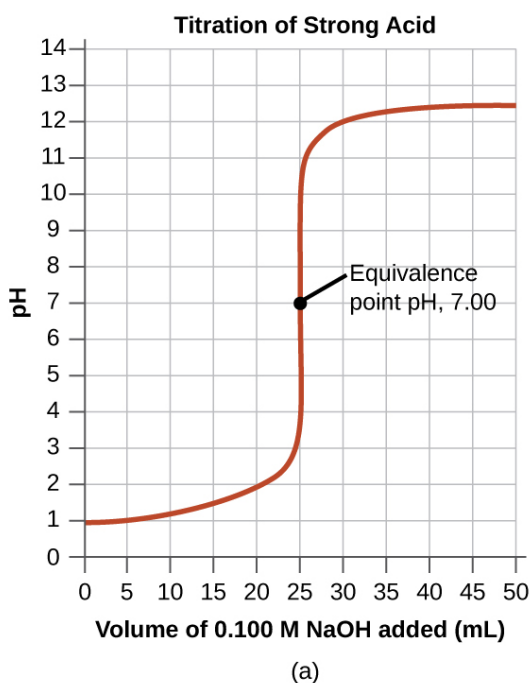
0.00: 1.000; 15.0: 1.5111; 25.0: 7; 40.0: 12.523

In the example, we calculated pH at four points during a titration. [\[link\]](#) shows a detailed sequence of changes in the pH of a strong acid and a weak acid in a titration with NaOH.

pH Values in the Titrations of a Strong Acid with a Strong Base and of a Weak Acid with a Strong Base

Volume of 0.100 M NaOH Added (mL)	Moles of NaOH Added	pH Values 0.100 M HCl^[footnote] Titration of 25.00 mL of 0.100 M HCl (0.00250 mol of HCl) with 0.100 M NaOH.	pH Values 0.100 M CH₃CO₂H^[footnote] Titration of 25.00 mL of 0.100 M CH₃CO₂H (0.00250 mol of CH₃CO₂H) with 0.100 M NaOH.
0.0	0.0	1.00	2.87
5.0	0.00050	1.18	4.14
10.0	0.00100	1.37	4.57
15.0	0.00150	1.60	4.92
20.0	0.00200	1.95	5.35
22.0	0.00220	2.20	5.61
24.0	0.00240	2.69	6.13
24.5	0.00245	3.00	6.44
24.9	0.00249	3.70	7.14
25.0	0.00250	7.00	8.72
25.1	0.00251	10.30	10.30
25.5	0.00255	11.00	11.00
26.0	0.00260	11.29	11.29
28.0	0.00280	11.75	11.75
30.0	0.00300	11.96	11.96
35.0	0.00350	12.22	12.22
40.0	0.00400	12.36	12.36
45.0	0.00450	12.46	12.46
50.0	0.00500	12.52	12.52

The simplest acid-base reactions are those of a strong acid with a strong base. [\[link\]](#) shows data for the titration of a 25.0-mL sample of 0.100 *M* hydrochloric acid with 0.100 *M* sodium hydroxide. The values of the pH measured after successive additions of small amounts of NaOH are listed in the first column of this table, and are graphed in [\[link\]](#), in a form that is called a **titration curve**. The pH increases slowly at first, increases rapidly in the middle portion of the curve, and then increases slowly again. The point of inflection (located at the midpoint of the vertical part of the curve) is observed when the amount of base added is equivalent to the amount of acid in the sample according to the stoichiometry of the titration reaction. The volume of titrant containing this stoichiometric amount of base is called the equivalence point for the titration (see the earlier chapter on stoichiometry). For the titration of a strong acid with a strong base, the equivalence point occurs at a pH of 7.00 and the points on the titration curve can be calculated using solution stoichiometry ([\[link\]](#) and [\[link\]](#)).

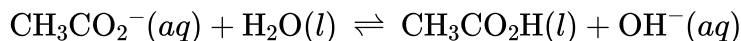


(a) The titration curve for the titration of 25.00 mL of 0.100 *M* HCl (strong acid) with 0.100 *M* NaOH (strong base) has an equivalence point of 7.00 pH. (b) The titration curve for the titration of 25.00 mL of 0.100 *M* acetic acid (weak acid) with 0.100 *M* NaOH (strong base) has an equivalence point of 8.72 pH.

The titration of a weak acid with a strong base (or of a weak base with a strong acid) is somewhat more complicated than that just discussed, but it follows the same general principles. Let us consider the titration of 25.0 mL of 0.100 *M* acetic acid (a weak acid) with 0.100 *M* sodium hydroxide and compare the titration curve with that of the strong acid. [\[link\]](#) gives the pH values during the titration, [\[link\]](#) shows the titration curve.

Although the initial volume and molarity of the acids are the same, there are important differences between the two titration curves. The titration curve for the weak acid begins at a higher value (less acidic) and maintains higher pH values up to the equivalence point. This is because acetic acid is a weak acid, which is only partially ionized. The pH at the equivalence point is also higher (8.72 rather than 7.00) due to the hydrolysis of acetate, a weak base that raises the pH:

Equation:



After the equivalence point, the two curves are identical because the pH is dependent on the excess of hydroxide ion in both cases.

Example:

Titration of a Weak Acid with a Strong Base

The titration curve shown in [\[link\]](#) is for the titration of 25.00 mL of 0.100 M $\text{CH}_3\text{CO}_2\text{H}$ with 0.100 M NaOH. The reaction can be represented as:

Equation:



- (a) What is the initial pH before any amount of the NaOH solution has been added? $K_a = 1.8 \times 10^{-5}$ for $\text{CH}_3\text{CO}_2\text{H}$.
- (b) Find the pH after 25.00 mL of the NaOH solution have been added.
- (c) Find the pH after 12.50 mL of the NaOH solution has been added.
- (d) Find the pH after 37.50 mL of the NaOH solution has been added.

Solution

(a) Assuming that the dissociated amount is small compared to 0.100 M, we find that:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} \approx \frac{[\text{H}_3\text{O}^+]^2}{[\text{CH}_3\text{CO}_2\text{H}]_0}, \text{ and}$$

$$[\text{H}_3\text{O}^+] = \sqrt{K_a \times [\text{CH}_3\text{CO}_2\text{H}]} = \sqrt{1.8 \times 10^{-5} \times 0.100} = 1.3 \times 10^{-3}$$

Equation:

$$\text{pH} = -\log(1.3 \times 10^{-3}) = 2.87$$

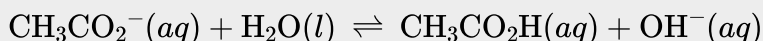
(b) After 25.00 mL of NaOH are added, the number of moles of NaOH and $\text{CH}_3\text{CO}_2\text{H}$ are equal because the amounts of the solutions and their concentrations are the same. All of the $\text{CH}_3\text{CO}_2\text{H}$ has been converted to CH_3CO_2^- . The concentration of the CH_3CO_2^- ion is:

Equation:

$$\frac{0.00250 \text{ mol}}{0.0500 \text{ L}} = 0.0500 \text{ MCH}_3\text{CO}_2^-$$

The equilibrium that must be focused on now is the basicity equilibrium for CH_3CO_2^- :

Equation:



so we must determine K_b for the base by using the ion product constant for water:

Equation:

$$K_b = \frac{[\text{CH}_3\text{CO}_2\text{H}][\text{OH}^-]}{[\text{CH}_3\text{CO}_2^-]}$$

Equation:

$$K_a = \frac{[\text{CH}_3\text{CO}_2^-][\text{H}^+]}{[\text{CH}_3\text{CO}_2\text{H}]}, \text{ so } \frac{[\text{CH}_3\text{CO}_2\text{H}]}{[\text{CH}_3\text{CO}_2^-]} = \frac{[\text{H}^+]}{K_a}.$$

Since $K_w = [\text{H}^+][\text{OH}^-]$:

Equation:

$$K_b = \frac{[\text{H}^+][\text{OH}^-]}{K_a} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Let us denote the concentration of each of the products of this reaction, $\text{CH}_3\text{CO}_2\text{H}$ and OH^- , as x . Using the assumption that x is small compared to 0.0500 M , $K_b = \frac{x^2}{0.0500 \text{ M}}$, and then:

Equation:

$$x = [\text{OH}^-] = 5.3 \times 10^{-6}$$

Equation:

$$\text{pOH} = -\log(5.3 \times 10^{-6}) = 5.28$$

Equation:

$$\text{pH} = 14.00 - 5.28 = 8.72$$

Note that the pH at the equivalence point of this titration is significantly greater than 7.

(c) In (b), 25.00 mL of the NaOH solution was added, and so practically all the $\text{CH}_3\text{CO}_2\text{H}$ was converted into CH_3CO_2^- . In this case, only 12.50 mL of the base solution has been introduced, and so only half of all the $\text{CH}_3\text{CO}_2\text{H}$ is converted into CH_3CO_2^- . The total initial number of moles of $\text{CH}_3\text{CO}_2\text{H}$ is $0.02500 \text{ L} \times 0.100 \text{ M} = 0.00250 \text{ mol}$, and so after adding the NaOH , the numbers of moles of $\text{CH}_3\text{CO}_2\text{H}$ and CH_3CO_2^- are both approximately equal to $\frac{0.00250 \text{ mol}}{2} = 0.00125 \text{ mol}$, and their concentrations are the same.

Since the amount of the added base is smaller than the original amount of the acid, the equivalence point has not been reached, the solution remains a buffer, and we can use the Henderson-Hasselbalch equation:

Equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Base}]}{[\text{Acid}]} = -\log(K_a) + \log \frac{[\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = -\log(1.8 \times 10^{-5}) + \log(1)$$

(as the concentrations of CH_3CO_2^- and $\text{CH}_3\text{CO}_2\text{H}$ are the same)

Thus:

Equation:

$$\text{pH} = -\log(1.8 \times 10^{-5}) = 4.74$$

(the pH = the pK_a at the halfway point in a titration of a weak acid)

(d) After 37.50 mL of NaOH is added, the amount of NaOH is $0.03750 \text{ L} \times 0.100 \text{ M} = 0.003750 \text{ mol}$ NaOH. Since this is past the equivalence point, the excess hydroxide ions will make the solution basic, and we can again use stoichiometric calculations to determine the pH:

Equation:

$$[\text{OH}^-] = \frac{(0.003750 \text{ mol} - 0.00250 \text{ mol})}{0.06250 \text{ L}} = 2.00 \times 10^{-2} \text{ M}$$

So:

Equation:

$$\text{pOH} = -\log(2.00 \times 10^{-2}) = 1.70, \text{ and } \text{pH} = 14.00 - 1.70 = 12.30$$

Note that this result is the same as for the strong acid-strong base titration example provided, since the amount of the strong base added moves the solution past the equivalence point.

Check Your Learning

Calculate the pH for the weak acid/strong base titration between 50.0 mL of 0.100 M $\text{HCOOH}(aq)$ (formic acid) and 0.200 M NaOH (titrant) at the listed volumes of added base: 0.00 mL, 15.0 mL, 25.0 mL, and 30.0 mL.

Note:**Answer:**

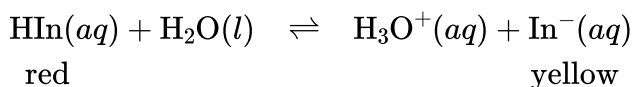
0.00 mL: 2.37; 15.0 mL: 3.92; 25.00 mL: 8.29; 30.0 mL: 12.097

Acid-Base Indicators

Certain organic substances change color in dilute solution when the hydronium ion concentration reaches a particular value. For example, phenolphthalein is a colorless substance in any aqueous solution with a hydronium ion concentration greater than $5.0 \times 10^{-9} \text{ M}$ ($\text{pH} < 8.3$). In more basic solutions where the hydronium ion concentration is less than $5.0 \times 10^{-9} \text{ M}$ ($\text{pH} > 8.3$), it is red or pink. Substances such as phenolphthalein, which can be used to determine the pH of a solution, are called **acid-base indicators**. Acid-base indicators are either weak organic acids or weak organic bases.

The equilibrium in a solution of the acid-base indicator methyl orange, a weak acid, can be represented by an equation in which we use HIn as a simple representation for the complex methyl orange molecule:

Equation:



Equation:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} = 4.0 \times 10^{-4}$$

The anion of methyl orange, In^- , is yellow, and the nonionized form, HIn , is red. When we add acid to a solution of methyl orange, the increased hydronium ion concentration shifts the equilibrium toward the nonionized red form, in accordance with Le Châtelier's principle. If we add base, we shift the equilibrium towards the yellow form. This behavior is completely analogous to the action of buffers.

An indicator's color is the visible result of the ratio of the concentrations of the two species In^- and HIn . If most of the indicator (typically about 60–90% or more) is present as In^- , then we see the color of the In^- ion, which would be yellow for methyl orange. If most is present as HIn , then we see the color of the HIn molecule: red for methyl orange. For methyl orange, we can rearrange the equation for K_a and write:

Equation:

$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{[\text{substance with yellow color}]}{[\text{substance with red color}]} = \frac{K_a}{[\text{H}_3\text{O}^+]}$$

This shows us how the ratio of $\frac{[\text{In}^-]}{[\text{HIn}]}$ varies with the concentration of hydronium ion.

The above expression describing the indicator equilibrium can be rearranged:

Equation:

$$\frac{[\text{H}_3\text{O}^+]}{K_a} = \frac{[\text{HIn}]}{[\text{In}^-]}$$

Equation:

$$\log\left(\frac{[\text{H}_3\text{O}^+]}{K_a}\right) = \log\left(\frac{[\text{HIn}]}{[\text{In}^-]}\right)$$

Equation:

$$\log([\text{H}_3\text{O}^+]) - \log(K_a) = -\log\left(\frac{[\text{In}^-]}{[\text{HIn}]}\right)$$

Equation:

$$-\text{pH} + \text{p}K_{\text{a}} = -\log\left(\frac{[\text{In}^-]}{[\text{HIn}]}\right)$$

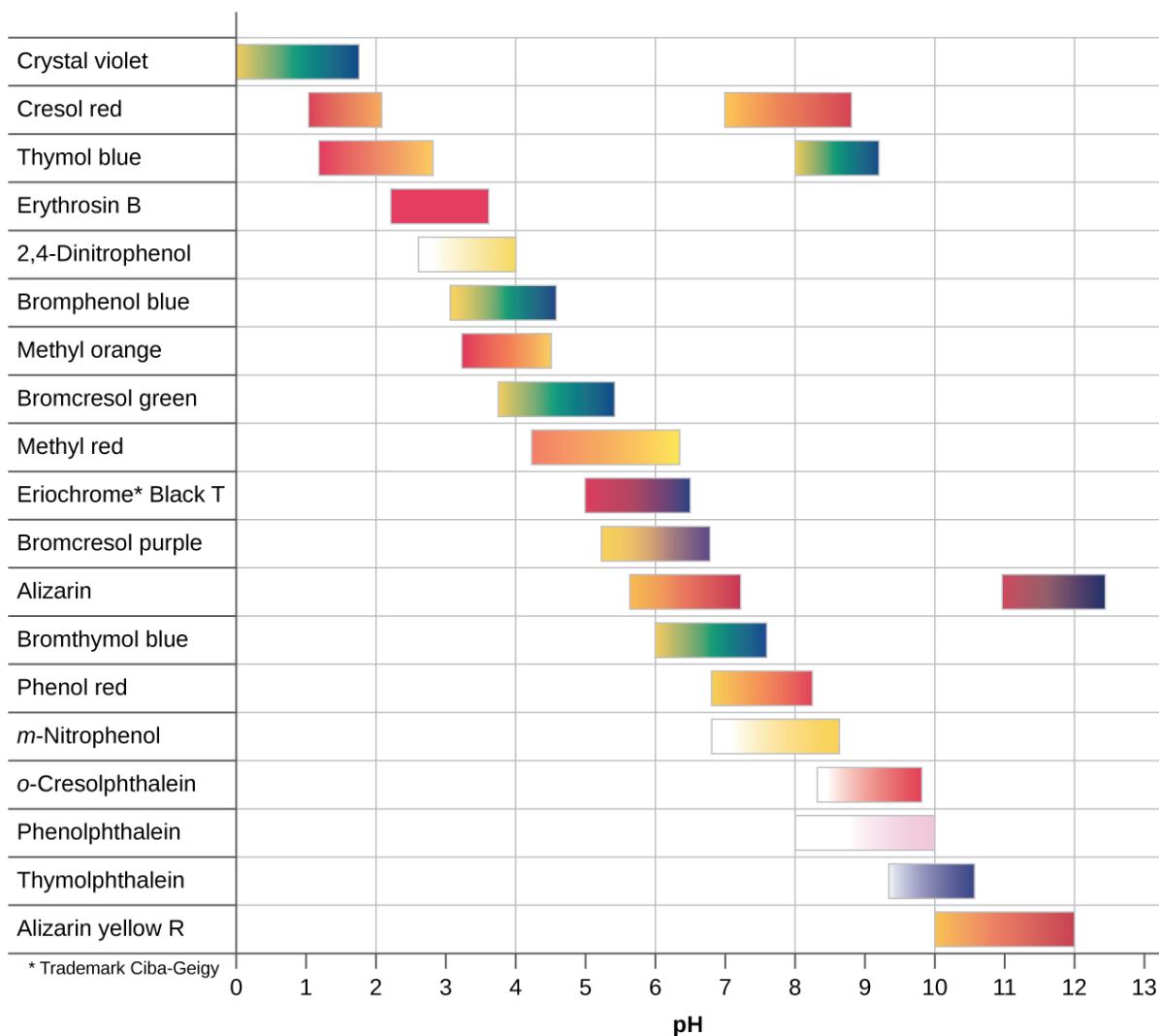
Equation:

$$\text{pH} = \text{p}K_{\text{a}} + \log\left(\frac{[\text{In}^-]}{[\text{HIn}]}\right) \text{ or } \text{pH} = \text{p}K_{\text{a}} + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$$

The last formula is the same as the Henderson-Hasselbalch equation, which can be used to describe the equilibrium of indicators.

When $[\text{H}_3\text{O}^+]$ has the same numerical value as K_{a} , the ratio of $[\text{In}^-]$ to $[\text{HIn}]$ is equal to 1, meaning that 50% of the indicator is present in the red form (HIn) and 50% is in the yellow ionic form (In^-), and the solution appears orange in color. When the hydronium ion concentration increases to $8 \times 10^{-4} \text{ M}$ (a pH of 3.1), the solution turns red. No change in color is visible for any further increase in the hydronium ion concentration (decrease in pH). At a hydronium ion concentration of $4 \times 10^{-5} \text{ M}$ (a pH of 4.4), most of the indicator is in the yellow ionic form, and a further decrease in the hydronium ion concentration (increase in pH) does not produce a visible color change. The pH range between 3.1 (red) and 4.4 (yellow) is the **color-change interval** of methyl orange; the pronounced color change takes place between these pH values.

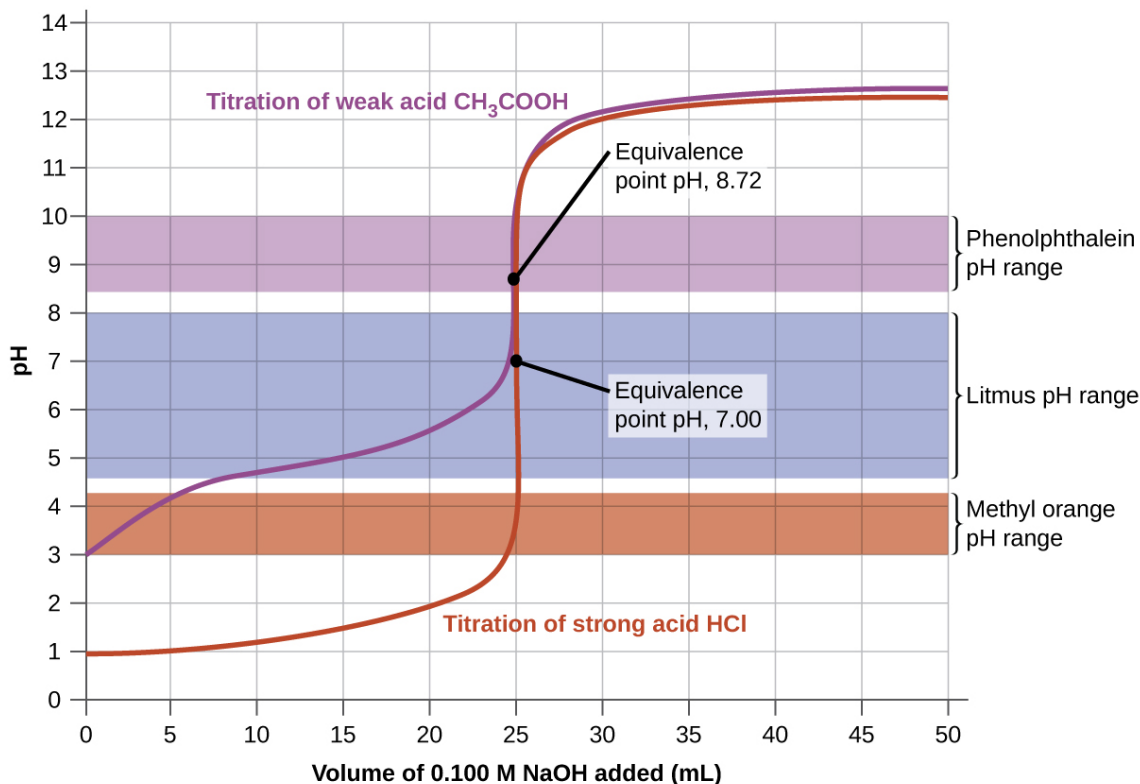
There are many different acid-base indicators that cover a wide range of pH values and can be used to determine the approximate pH of an unknown solution by a process of elimination. Universal indicators and pH paper contain a mixture of indicators and exhibit different colors at different pHs. [\[link\]](#) presents several indicators, their colors, and their color-change intervals.



This chart illustrates the ranges of color change for several acid-base indicators.

Titration curves help us pick an indicator that will provide a sharp color change at the equivalence point. The best selection would be an indicator that has a color change interval that brackets the pH at the equivalence point of the titration.

Color change pH intervals for three different acid-base indicators are shown in [\[link\]](#). Since the phenolphthalein color change interval occurs within the near-vertical portions of both titrations curves, this indicator may be used to signal the end point in both strong and weak acid titrations.



The graph shows a titration curve for the titration of 25.00 mL of 0.100 M $\text{CH}_3\text{CO}_2\text{H}$ (weak acid) with 0.100 M NaOH (strong base) and the titration curve for the titration of HCl (strong acid) with NaOH (strong base). The pH ranges for the color change of phenolphthalein, litmus, and methyl orange are indicated by the shaded areas.

Litmus is a suitable indicator for the HCl titration because its color change brackets the equivalence point. However, we should not use litmus for the $\text{CH}_3\text{CO}_2\text{H}$ titration because the pH is within the color-change interval of litmus when only about 12 mL of NaOH has been added, and it does not leave the range until 25 mL has been added. The color change would be very gradual, taking place during the addition of 13 mL of NaOH, making litmus useless as an indicator of the equivalence point.

We could use methyl orange for the HCl titration, but it would not give very accurate results: (1) It completes its color change slightly before the equivalence point is reached (but very close to it, so this is not too serious); (2) it changes color, as [\[link\]](#) shows, during the addition of nearly 0.5 mL of NaOH, which is not so sharp a color change as that of litmus or phenolphthalein; and (3) it goes from yellow to orange to red, making detection of a precise endpoint much more challenging than the colorless to pink change of phenolphthalein. [\[link\]](#) shows us that methyl orange would be completely useless as an indicator for the $\text{CH}_3\text{CO}_2\text{H}$ titration. Its color change begins after about 1 mL of NaOH has been added and ends when about 8 mL has been added. The color change is completed long before the equivalence point (which occurs when 25.0 mL of NaOH has been added) is reached and hence provides no indication of the equivalence point.

We base our choice of indicator on a calculated pH, the pH at the equivalence point. At the equivalence point, equimolar amounts of acid and base have been mixed, and the calculation becomes that of the pH of a solution of the salt resulting from the titration.

Key Concepts and Summary

A titration curve is a graph that relates the change in pH of an acidic or basic solution to the volume of added titrant. The characteristics of the titration curve are dependent on the specific solutions being titrated. The pH of the solution at the equivalence point may be greater than, equal to, or less than 7.00. The choice of an indicator for a given titration depends on the expected pH at the equivalence point of the titration, and the range of the color change of the indicator.

Exercise:

Problem:

Explain how to choose the appropriate acid-base indicator for the titration of a weak base with a strong acid.

Solution:

At the equivalence point in the titration of a weak base with a strong acid, the resulting solution is slightly acidic due to the presence of the conjugate acid. Thus, pick an indicator that changes color in the acidic range and brackets the pH at the equivalence point. Methyl orange is a good example.

Exercise:

Problem:

Explain why an acid-base indicator changes color over a range of pH values rather than at a specific pH.

Exercise:

Problem:

Why can we ignore the contribution of water to the concentrations of H_3O^+ in the solutions of following acids:

0.0092 M HClO , a weak acid

0.0810 M HCN , a weak acid

0.120 M $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ a weak acid, $K_a = 1.6 \times 10^{-7}$

but not the contribution of water to the concentration of OH^- ?

Solution:

In an acid solution, the only source of OH^- ions is water. We use K_w to calculate the concentration. If the contribution from water was neglected, the concentration of OH^- would

be zero.

Exercise:

Problem:

Why can we ignore the contribution of water to the concentration of OH^- in a solution of the following bases:

0.0784 M $\text{C}_6\text{H}_5\text{NH}_2$, a weak base

0.11 M $(\text{CH}_3)_3\text{N}$, a weak base

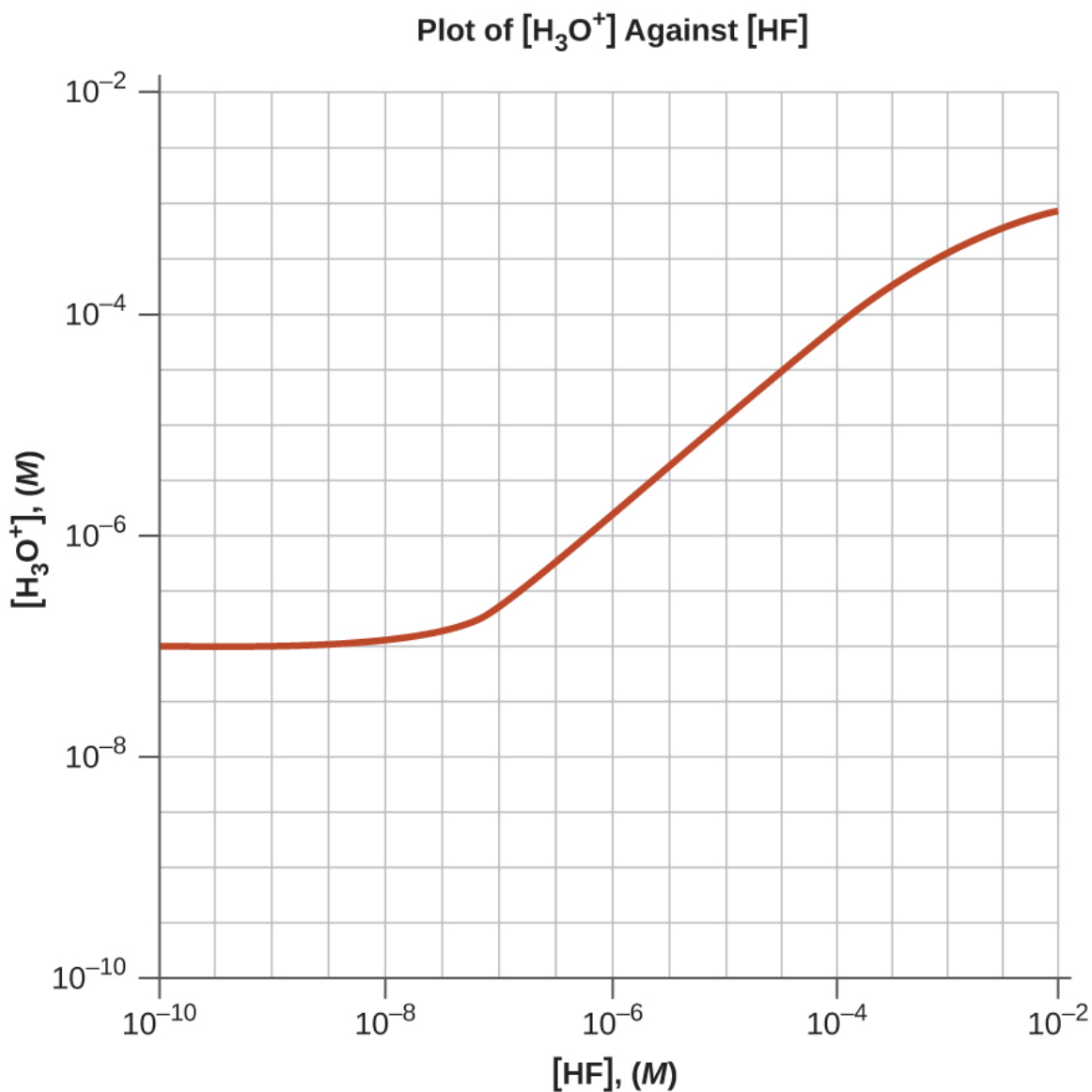
but not the contribution of water to the concentration of H_3O^+ ?

Exercise:

Problem:

Draw a curve for a series of solutions of HF. Plot $[\text{H}_3\text{O}^+]_{\text{total}}$ on the vertical axis and the total concentration of HF (the sum of the concentrations of both the ionized and nonionized HF molecules) on the horizontal axis. Let the total concentration of HF vary from $1 \times 10^{-10} \text{ M}$ to $1 \times 10^{-2} \text{ M}$.

Solution:



Exercise:

Problem:

Draw a curve similar to that shown in [\[link\]](#) for a series of solutions of NH_3 . Plot $[\text{OH}^-]$ on the vertical axis and the total concentration of NH_3 (both ionized and nonionized NH_3 molecules) on the horizontal axis. Let the total concentration of NH_3 vary from $1 \times 10^{-10} M$ to $1 \times 10^{-2} M$.

Exercise:

Problem:

Calculate the pH at the following points in a titration of 40 mL (0.040 L) of 0.100 M barbituric acid ($K_a = 9.8 \times 10^{-5}$) with 0.100 M KOH.

- (a) no KOH added
 - (b) 20 mL of KOH solution added
 - (c) 39 mL of KOH solution added
 - (d) 40 mL of KOH solution added
 - (e) 41 mL of KOH solution added
-

Solution:

- (a) pH = 2.50;
- (b) pH = 4.01;
- (c) pH = 5.60;
- (d) pH = 8.35;
- (e) pH = 11.08

Exercise:

Problem:

The indicator dinitrophenol is an acid with a K_a of 1.1×10^{-4} . In a 1.0×10^{-4} -M solution, it is colorless in acid and yellow in base. Calculate the pH range over which it goes from 10% ionized (colorless) to 90% ionized (yellow).

Glossary

acid-base indicator

organic acid or base whose color changes depending on the pH of the solution it is in

color-change interval

range in pH over which the color change of an indicator takes place

titration curve

plot of the pH of a solution of acid or base versus the volume of base or acid added during a titration

Introduction

class="introduction"

- Spontaneity
- Entropy
- The Second and Third Laws of Thermodynamics
- Free Energy

Geysers are a dramatic display of thermodynamic principles in nature. As water inside the earth heats up, it rises to the surface through small channels.

Pressure builds up until the water turns to steam, and steam is expelled forcefully through a hole at the surface.

(credit: modification of work by Yellowstone National Park)



Among the many capabilities of chemistry is its ability to predict if a process will occur under specified conditions. Thermodynamics, the study of relationships between the energy and work associated with chemical and physical processes, provides this predictive ability. Previous chapters in this text have described various applications of thermochemistry, an important aspect of thermodynamics concerned with the heat flow accompanying chemical reactions and phase transitions. This chapter will introduce additional thermodynamic concepts, including those that enable the prediction of any chemical or physical changes under a given set of conditions.

Spontaneity

By the end of this section, you will be able to:

- Distinguish between spontaneous and nonspontaneous processes
- Describe the dispersal of matter and energy that accompanies certain spontaneous processes

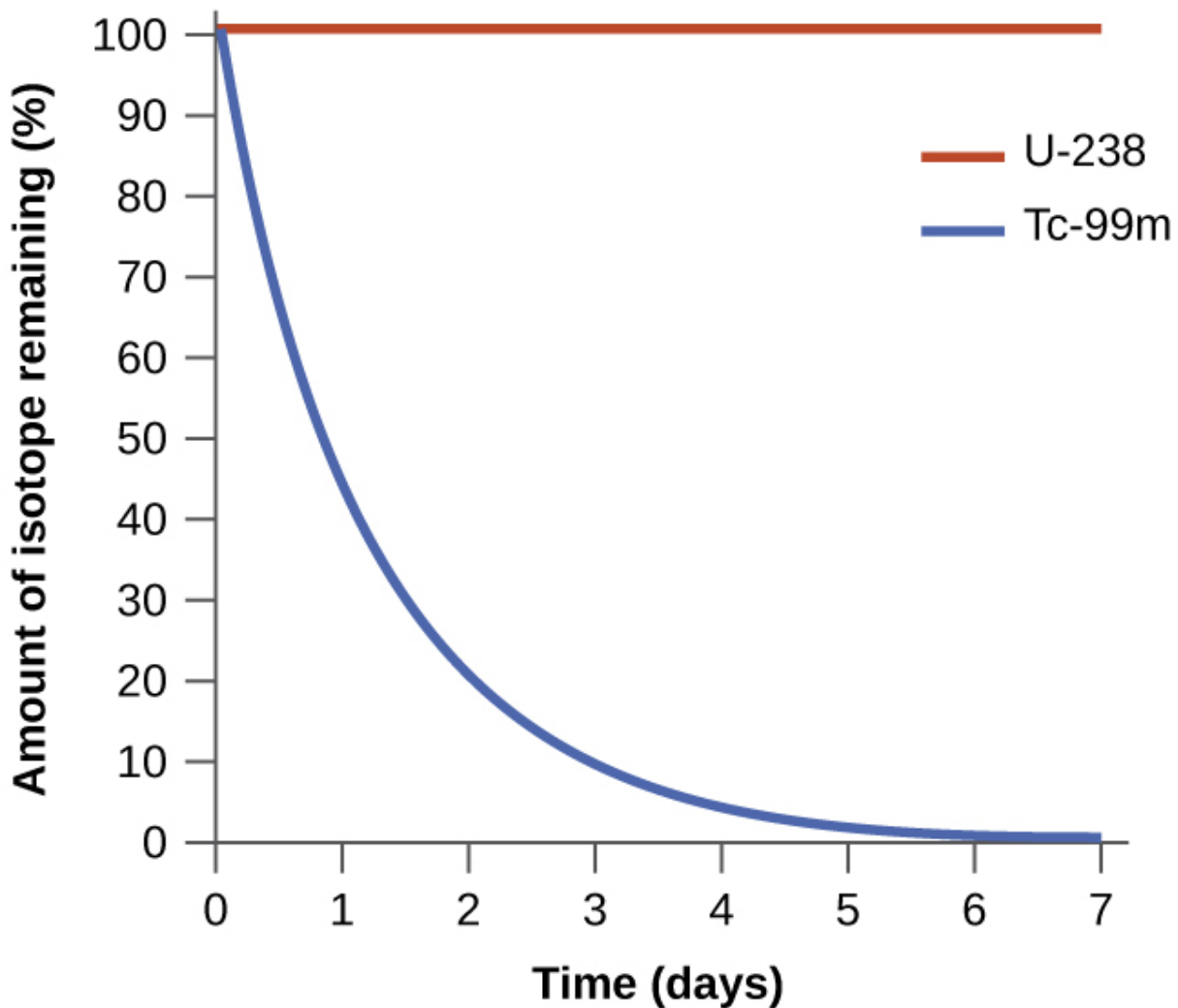
In this section, consider the differences between two types of changes in a system: Those that occur spontaneously and those that occur by force. In doing so, we'll gain an understanding as to why some systems are naturally inclined to change in one direction under certain conditions and how relatively quickly or slowly that natural change proceeds. We'll also gain insight into how the spontaneity of a process affects the distribution of energy and matter within the system.

Spontaneous and Nonspontaneous Processes

Processes have a natural tendency to occur in one direction under a given set of conditions. Water will naturally flow downhill, but uphill flow requires outside intervention such as the use of a pump. Iron exposed to the earth's atmosphere will corrode, but rust is not converted to iron without intentional chemical treatment. A **spontaneous process** is one that occurs naturally under certain conditions. A **nonspontaneous process**, on the other hand, will not take place unless it is "driven" by the continual input of energy from an external source. A process that is spontaneous in one direction under a particular set of conditions is nonspontaneous in the reverse direction. At room temperature and typical atmospheric pressure, for example, ice will spontaneously melt, but water will not spontaneously freeze.

The spontaneity of a process is *not* correlated to the speed of the process. A spontaneous change may be so rapid that it is essentially instantaneous or so slow that it cannot be observed over any practical period of time. To illustrate this concept, consider the decay of radioactive isotopes, a topic more thoroughly treated in the chapter on nuclear chemistry. Radioactive decay is by definition a spontaneous process in which the nuclei of unstable isotopes emit radiation as they are converted to more stable nuclei. All the

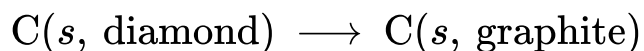
decay processes occur spontaneously, but the rates at which different isotopes decay vary widely. Technetium-99m is a popular radioisotope for medical imaging studies that undergoes relatively rapid decay and exhibits a half-life of about six hours. Uranium-238 is the most abundant isotope of uranium, and its decay occurs much more slowly, exhibiting a half-life of more than four billion years ([\[link\]](#)).



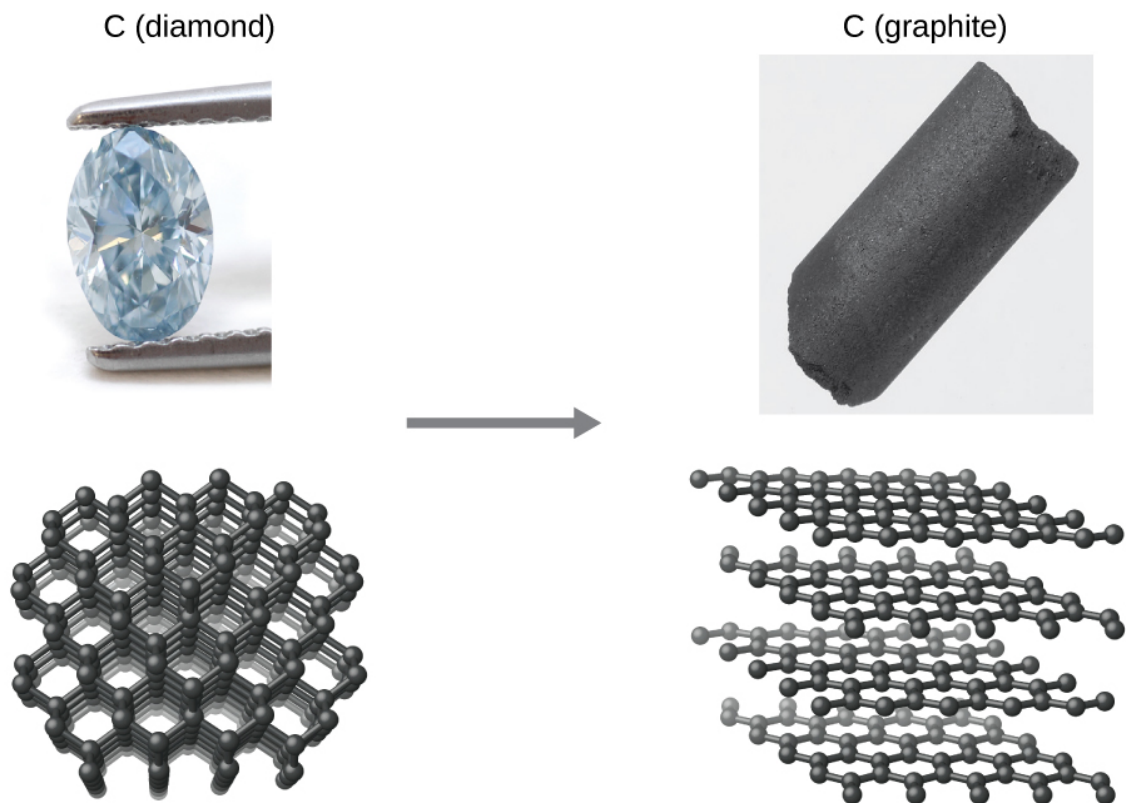
Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed.

As another example, consider the conversion of diamond into graphite ([link](#)).

Equation:



The phase diagram for carbon indicates that graphite is the stable form of this element under ambient atmospheric pressure, while diamond is the stable allotrope at very high pressures, such as those present during its geologic formation. Thermodynamic calculations of the sort described in the last section of this chapter indicate that the conversion of diamond to graphite at ambient pressure occurs spontaneously, yet diamonds are observed to exist, and persist, under these conditions. Though the process is spontaneous under typical ambient conditions, its rate is extremely slow, and so for all practical purposes diamonds are indeed “forever.” Situations such as these emphasize the important distinction between the thermodynamic and the kinetic aspects of a process. In this particular case, diamonds are said to be *thermodynamically unstable* but *kinetically stable* under ambient conditions.



The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as *graphitization*, and its rate can be increased to easily measurable values at temperatures in the 1000–2000 K range. (credit "diamond" photo: modification of work by "Fancy Diamonds"/Flickr; credit "graphite" photo: modification of work by images-of-elements.com/carbon.php)

Dispersal of Matter and Energy

As we extend our discussion of thermodynamic concepts toward the objective of predicting spontaneity, consider now an isolated system consisting of two flasks connected with a closed valve. Initially there is an ideal gas on the left and a vacuum on the right ([link](#)). When the valve is opened, the gas spontaneously expands to fill both flasks. Recalling the

definition of pressure-volume work from the chapter on thermochemistry, note that no work has been done because the pressure in a vacuum is zero.

Equation:

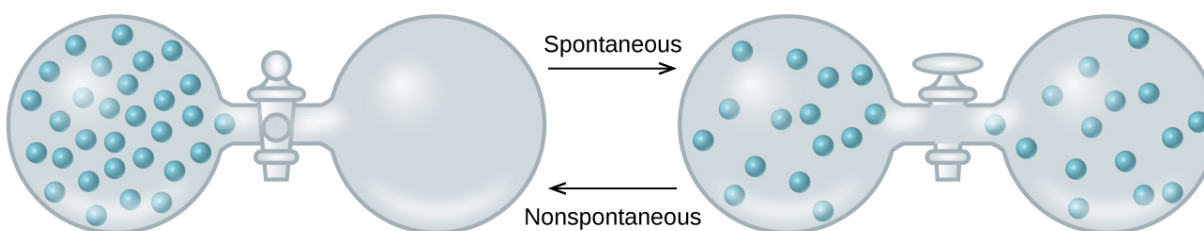
$$w = -P\Delta V = 0 \quad (P = 0 \text{ in a vacuum})$$

Note as well that since the system is isolated, no heat has been exchanged with the surroundings ($q = 0$). The first law of thermodynamics confirms that there has been no change in the system's internal energy as a result of this process.

Equation:

$$\Delta U = q + w = 0 + 0 = 0$$

The spontaneity of this process is therefore not a consequence of any change in energy that accompanies the process. Instead, the driving force appears to be related to the *greater, more uniform dispersal of matter* that results when the gas is allowed to expand. Initially, the system was comprised of one flask containing matter and another flask containing nothing. After the spontaneous process took place, the matter was distributed both more widely (occupying twice its original volume) and more uniformly (present in equal amounts in each flask).



An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

Now consider two objects at different temperatures: object X at temperature T_X and object Y at temperature T_Y , with $T_X > T_Y$ ([link](#)). When these objects come into contact, heat spontaneously flows from the hotter object (X) to the colder one (Y). This corresponds to a loss of thermal energy by X and a gain of thermal energy by Y.

Equation:

$$q_X < 0 \quad \text{and} \quad q_Y = -q_X > 0$$

From the perspective of this two-object system, there was no net gain or loss of thermal energy, rather the available thermal energy was redistributed among the two objects. This spontaneous process resulted in a *more uniform dispersal of energy*.



When two objects at different temperatures come in contact, heat spontaneously flows from the hotter to the colder object.

As illustrated by the two processes described, an important factor in determining the spontaneity of a process is the extent to which it changes the dispersal or distribution of matter and/or energy. In each case, a spontaneous process took place that resulted in a more uniform distribution of matter or energy.

Example:**Redistribution of Matter during a Spontaneous Process**

Describe how matter is redistributed when the following spontaneous processes take place:

- (a) A solid sublimates.
- (b) A gas condenses.
- (c) A drop of food coloring added to a glass of water forms a solution with uniform color.

Solution

(a)



(b)



(c)

(credit a: modification of work by Jenny Downing; credit b: modification of work by “Fuzzy Gerdes”/Flickr; credit c: modification of work by Sahar Atwa)

(a) Sublimation is the conversion of a solid (relatively high density) to a gas (much lesser density). This process yields a much greater dispersal of matter, since the molecules will occupy a much greater volume after the solid-to-gas transition.

(b) Condensation is the conversion of a gas (relatively low density) to a liquid (much greater density). This process yields a much lesser dispersal of matter, since the molecules will occupy a much lesser volume after the gas-to-liquid transition.

(c) The process in question is dilution. The food dye molecules initially occupy a much smaller volume (the drop of dye solution) than they occupy once the process is complete (in the full glass of water). The process therefore entails a greater dispersal of matter. The process may also yield a

more uniform dispersal of matter, since the initial state of the system involves two regions of different dye concentrations (high in the drop, zero in the water), and the final state of the system contains a single dye concentration throughout.

Check Your Learning

Describe how matter and/or energy is redistributed when you empty a canister of compressed air into a room.

Note:

Answer:

This is also a dilution process, analogous to example (c). It entails both a greater and more uniform dispersal of matter as the compressed air in the canister is permitted to expand into the lower-pressure air of the room.

Key Concepts and Summary

Chemical and physical processes have a natural tendency to occur in one direction under certain conditions. A spontaneous process occurs without the need for a continual input of energy from some external source, while a nonspontaneous process requires such. Systems undergoing a spontaneous process may or may not experience a gain or loss of energy, but they will experience a change in the way matter and/or energy is distributed within the system.

Chemistry End of Chapter Exercises

Exercise:

Problem: What is a spontaneous reaction?

Solution:

A reaction has a natural tendency to occur and takes place without the continual input of energy from an external source.

Exercise:

Problem: What is a nonspontaneous reaction?

Exercise:**Problem:**

Indicate whether the following processes are spontaneous or nonspontaneous.

- (a) Liquid water freezing at a temperature below its freezing point
- (b) Liquid water freezing at a temperature above its freezing point
- (c) The combustion of gasoline
- (d) A ball thrown into the air
- (e) A raindrop falling to the ground
- (f) Iron rusting in a moist atmosphere

Solution:

(a) spontaneous; (b) nonspontaneous; (c) spontaneous; (d) nonspontaneous; (e) spontaneous; (f) spontaneous

Exercise:**Problem:**

A helium-filled balloon spontaneously deflates overnight as He atoms diffuse through the wall of the balloon. Describe the redistribution of matter and/or energy that accompanies this process.

Exercise:**Problem:**

Many plastic materials are organic polymers that contain carbon and hydrogen. The oxidation of these plastics in air to form carbon dioxide and water is a spontaneous process; however, plastic materials tend to persist in the environment. Explain.

Solution:

Although the oxidation of plastics is spontaneous, the rate of oxidation is very slow. Plastics are therefore kinetically stable and do not decompose appreciably even over relatively long periods of time.

Glossary

nonspontaneous process

process that requires continual input of energy from an external source

spontaneous change

process that takes place without a continuous input of energy from an external source

Entropy

By the end of this section, you will be able to:

- Define entropy
- Explain the relationship between entropy and the number of microstates
- Predict the sign of the entropy change for chemical and physical processes

In 1824, at the age of 28, Nicolas Léonard Sadi Carnot ([\[link\]](#)) published the results of an extensive study regarding the efficiency of steam heat engines. In a later review of Carnot's findings, Rudolf Clausius introduced a new thermodynamic property that relates the spontaneous heat flow accompanying a process to the temperature at which the process takes place. This new property was expressed as the ratio of the *reversible* heat (q_{rev}) and the kelvin temperature (T). The term **reversible process** refers to a process that takes place at such a slow rate that it is always at equilibrium and its direction can be changed (it can be “reversed”) by an infinitesimally small change in some condition. Note that the idea of a reversible process is a formalism required to support the development of various thermodynamic concepts; no real processes are truly reversible, rather they are classified as *irreversible*.



(a)



(b)

(a) Nicholas Léonard Sadi Carnot's research into steam-powered machinery and (b) Rudolf Clausius's later study of those findings led to groundbreaking discoveries about spontaneous heat flow processes.

Similar to other thermodynamic properties, this new quantity is a state function, and so its change depends only upon the initial and final states of a system. In 1865, Clausius named this property **entropy (S)** and defined its change for any process as the following:

Equation:

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

The entropy change for a real, irreversible process is then equal to that for the theoretical reversible process that involves the same initial and final states.

Entropy and Microstates

Following the work of Carnot and Clausius, Ludwig Boltzmann developed a molecular-scale statistical model that related the entropy of a system to the number of *microstates* possible for the system. A **microstate (W)** is a specific configuration of the locations and energies of the atoms or molecules that comprise a system like the following:

Equation:

$$S = k \ln W$$

Here k is the Boltzmann constant and has a value of 1.38×10^{-23} J/K.

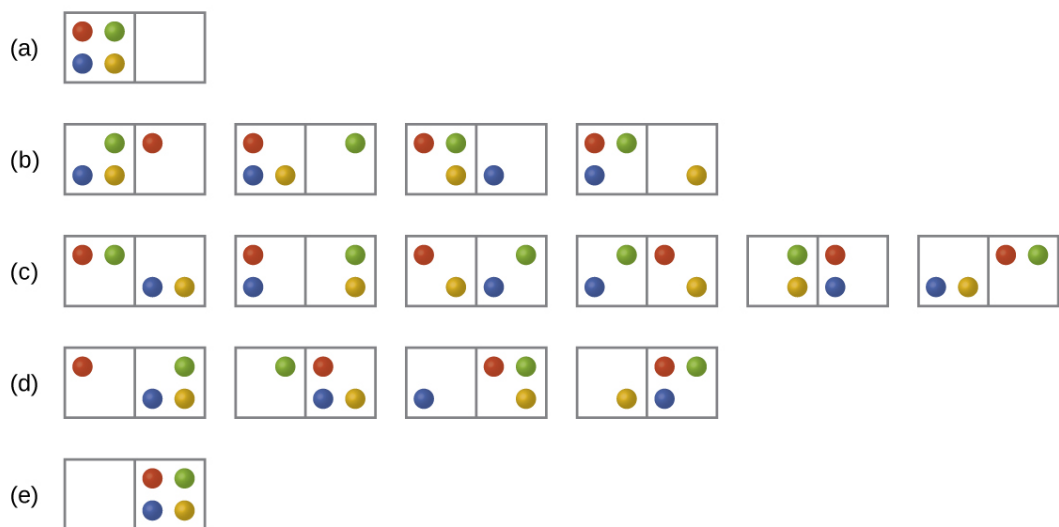
As for other state functions, the change in entropy for a process is the difference between its final (S_f) and initial (S_i) values:

Equation:

$$\Delta S = S_f - S_i = k \ln W_f - k \ln W_i = k \ln \frac{W_f}{W_i}$$

For processes involving an increase in the number of microstates, $W_f > W_i$, the entropy of the system increases, $\Delta S > 0$. Conversely, processes that reduce the number of microstates, $W_f < W_i$, yield a decrease in system entropy, $\Delta S < 0$. This molecular-scale interpretation of entropy provides a link to the probability that a process will occur as illustrated in the next paragraphs.

Consider the general case of a system comprised of N particles distributed among n boxes. The number of microstates possible for such a system is n^N . For example, distributing four particles among two boxes will result in $2^4 = 16$ different microstates as illustrated in [\[link\]](#). Microstates with equivalent particle arrangements (not considering individual particle identities) are grouped together and are called *distributions*. The probability that a system will exist with its components in a given distribution is proportional to the number of microstates within the distribution. Since entropy increases logarithmically with the number of microstates, *the most probable distribution is therefore the one of greatest entropy*.



The sixteen microstates associated with placing four particles in two boxes are shown. The microstates are collected into five distributions—(a), (b), (c), (d), and (e)—based on the numbers of particles in each box.

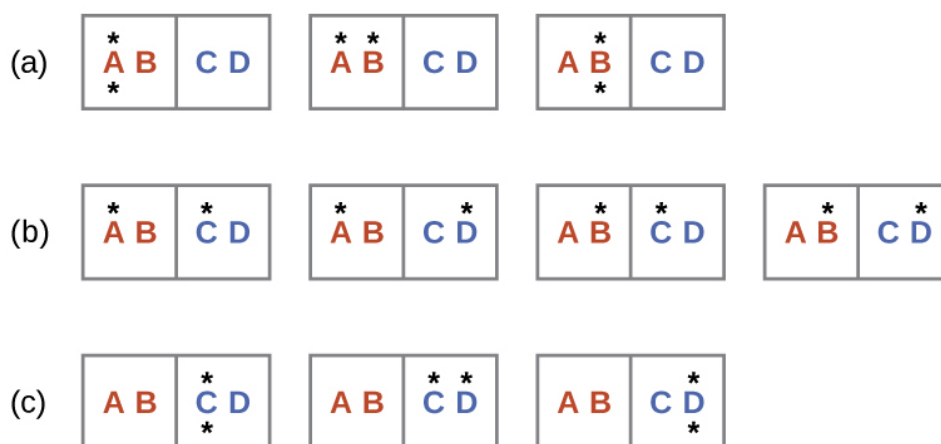
For this system, the most probable configuration is one of the six microstates associated with distribution (c) where the particles are evenly distributed between the boxes, that is, a configuration of two particles in each box. The probability of finding the system in this configuration is $\frac{6}{16}$ or $\frac{3}{8}$. The least probable configuration of the system is one in which all four particles are in one box, corresponding to distributions (a) and (e), each with a probability of $\frac{1}{16}$. The probability of finding all particles in only one box (either the left box or right box) is then $(\frac{1}{16} + \frac{1}{16}) = \frac{2}{16}$ or $\frac{1}{8}$.

As you add more particles to the system, the number of possible microstates increases exponentially (2^N). A macroscopic (laboratory-sized) system would typically consist of moles of particles ($N \sim 10^{23}$), and the corresponding number of microstates would be staggeringly huge. Regardless of the number of particles in the system, however, the distributions in which roughly equal numbers of particles are found in each box are always the most probable configurations.

The previous description of an ideal gas expanding into a vacuum ([link](#)) is a macroscopic example of this particle-in-a-box model. For this system, the most probable distribution is confirmed to be the one in which the matter is most uniformly dispersed or distributed between the two flasks. The spontaneous process whereby the gas contained initially in one flask expands to fill both flasks equally therefore yields an increase in entropy for the system.

A similar approach may be used to describe the spontaneous flow of heat. Consider a system consisting of two objects, each containing two particles, and two units of energy (represented as “*”) in [link](#). The hot object is comprised of particles **A** and **B** and initially contains both energy units. The cold object is comprised of particles **C** and **D**, which initially has no energy units. Distribution (a) shows the three microstates possible for the initial state of the system, with both units of energy contained within the hot object. If one of the two energy units is transferred, the result is distribution (b) consisting of four microstates. If both energy units are transferred, the result is distribution (c) consisting of three microstates. And so, we may describe this system by a total of ten microstates. The probability that the heat does not flow when the two objects are brought into contact, that is, that the system remains in distribution (a), is $\frac{3}{10}$. More likely is the flow of heat to yield one of the other

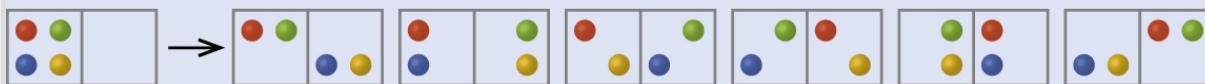
two distribution, the combined probability being $\frac{7}{10}$. The most likely result is the flow of heat to yield the uniform dispersal of energy represented by distribution (b), the probability of this configuration being $\frac{4}{10}$. As for the previous example of matter dispersal, extrapolating this treatment to macroscopic collections of particles dramatically increases the probability of the uniform distribution relative to the other distributions. This supports the common observation that placing hot and cold objects in contact results in spontaneous heat flow that ultimately equalizes the objects' temperatures. And, again, this spontaneous process is also characterized by an increase in system entropy.



This shows a microstate model describing the flow of heat from a hot object to a cold object. (a) Before the heat flow occurs, the object comprised of particles **A** and **B** contains both units of energy and as represented by a distribution of three microstates. (b) If the heat flow results in an even dispersal of energy (one energy unit transferred), a distribution of four microstates results. (c) If both energy units are transferred, the resulting distribution has three microstates.

Example: Determination of ΔS

Consider the system shown here. What is the change in entropy for a process that converts the system from distribution (a) to (c)?



Solution

We are interested in the following change:

The initial number of microstates is one, the final six:

Equation:

$$\Delta S = k \ln \frac{W_c}{W_a} = 1.38 \times 10^{-23} \text{ J/K} \times \ln \frac{6}{1} = 2.47 \times 10^{-23} \text{ J/K}$$

The sign of this result is consistent with expectation; since there are more microstates possible for the final state than for the initial state, the change in entropy should be positive.

Check Your Learning

Consider the system shown in [\[link\]](#). What is the change in entropy for the process where *all* the energy is transferred from the hot object (**AB**) to the cold object (**CD**)?

Note:

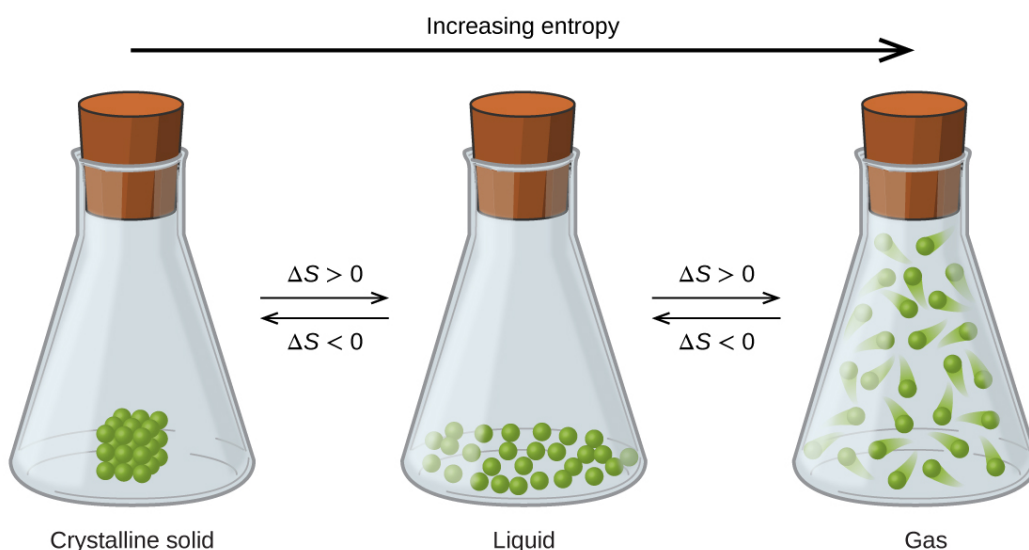
Answer:

0 J/K

Predicting the Sign of ΔS

The relationships between entropy, microstates, and matter/energy dispersal described previously allow us to make generalizations regarding the relative entropies of substances and to predict the sign of entropy changes for chemical and physical processes. Consider the phase changes illustrated in [\[link\]](#). In the

solid phase, the atoms or molecules are restricted to nearly fixed positions with respect to each other and are capable of only modest oscillations about these positions. With essentially fixed locations for the system's component particles, the number of microstates is relatively small. In the liquid phase, the atoms or molecules are free to move over and around each other, though they remain in relatively close proximity to one another. This increased freedom of motion results in a greater variation in possible particle locations, so the number of microstates is correspondingly greater than for the solid. As a result, $S_{\text{liquid}} > S_{\text{solid}}$ and the process of converting a substance from solid to liquid (melting) is characterized by an increase in entropy, $\Delta S > 0$. By the same logic, the reciprocal process (freezing) exhibits a decrease in entropy, $\Delta S < 0$.

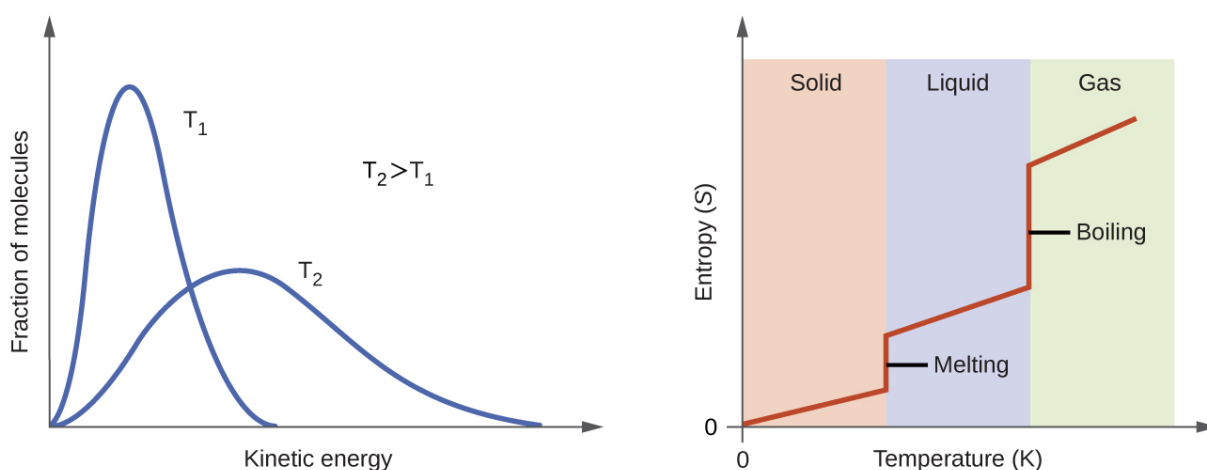


The entropy of a substance increases ($\Delta S > 0$) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases ($\Delta S < 0$) as the substance transforms from a gas to a liquid and then to a solid.

Now consider the vapor or gas phase. The atoms or molecules occupy a *much* greater volume than in the liquid phase; therefore each atom or molecule can be found in many more locations than in the liquid (or solid) phase.

Consequently, for any substance, $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$, and the processes of vaporization and sublimation likewise involve increases in entropy, $\Delta S > 0$. Likewise, the reciprocal phase transitions, condensation and deposition, involve decreases in entropy, $\Delta S < 0$.

According to kinetic-molecular theory, the temperature of a substance is proportional to the average kinetic energy of its particles. Raising the temperature of a substance will result in more extensive vibrations of the particles in solids and more rapid translations of the particles in liquids and gases. At higher temperatures, the distribution of kinetic energies among the atoms or molecules of the substance is also broader (more dispersed) than at lower temperatures. Thus, the entropy for any substance increases with temperature ([link](#)).



Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance melts or vaporizes, it experiences a significant increase in entropy.

Note:



Try this [simulator](#) with interactive visualization of the dependence of particle location and freedom of motion on physical state and temperature.

The entropy of a substance is influenced by the structure of the particles (atoms or molecules) that comprise the substance. With regard to atomic substances, heavier atoms possess greater entropy at a given temperature than lighter atoms, which is a consequence of the relation between a particle's mass and the spacing of quantized translational energy levels (which is a topic beyond the scope of our treatment). For molecules, greater numbers of atoms (regardless of their masses) increase the number of ways in which the molecules can vibrate and thus the number of possible microstates and the entropy of the system.

Finally, variations in the types of particles affects the entropy of a system. Compared to a pure substance, in which all particles are identical, the entropy of a mixture of two or more different particle types is greater. This is because of the additional orientations and interactions that are possible in a system comprised of nonidentical components. For example, when a solid dissolves in a liquid, the particles of the solid experience both a greater freedom of motion and additional interactions with the solvent particles. This corresponds to a more uniform dispersal of matter and energy and a greater number of microstates. The process of dissolution therefore involves an increase in entropy, $\Delta S > 0$.

Considering the various factors that affect entropy allows us to make informed predictions of the sign of ΔS for various chemical and physical processes as illustrated in [\[link\]](#).

Example:**Predicting the Sign of ΔS**

Predict the sign of the entropy change for the following processes. Indicate the reason for each of your predictions.

(a) One mole liquid water at room temperature \longrightarrow one mole liquid water at 50 °C

(b) $\text{Ag}^+(aq) + \text{Cl}^-(aq) \longrightarrow \text{AgCl}(s)$

(c) $\text{C}_6\text{H}_6(l) + \frac{15}{2} \text{O}_2(g) \longrightarrow 6\text{CO}_2(g) + 3\text{H}_2\text{O}(l)$

(d) $\text{NH}_3(s) \longrightarrow \text{NH}_3(l)$

Solution

(a) positive, temperature increases

(b) negative, reduction in the number of ions (particles) in solution, decreased dispersal of matter

(c) negative, net decrease in the amount of gaseous species

(d) positive, phase transition from solid to liquid, net increase in dispersal of matter

Check Your Learning

Predict the sign of the enthalpy change for the following processes. Give a reason for your prediction.

(a) $\text{NaNO}_3(s) \longrightarrow \text{Na}^+(aq) + \text{NO}_3^-(aq)$

(b) the freezing of liquid water

(c) $\text{CO}_2(s) \longrightarrow \text{CO}_2(g)$

(d) $\text{CaCO}(s) \longrightarrow \text{CaO}(s) + \text{CO}_2(g)$

Note:**Answer:**

(a) Positive; The solid dissolves to give an increase of mobile ions in solution. (b) Negative; The liquid becomes a more ordered solid. (c) Positive; The relatively ordered solid becomes a gas. (d) Positive; There is a net production of one mole of gas.

Key Concepts and Summary

Entropy (S) is a state function that can be related to the number of microstates for a system (the number of ways the system can be arranged) and to the ratio of reversible heat to kelvin temperature. It may be interpreted as a measure of the dispersal or distribution of matter and/or energy in a system, and it is often described as representing the “disorder” of the system.

For a given substance, its entropy depends on its phase with $S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$. For different substances in the same physical state at a given temperature, entropy is typically greater for heavier atoms or more complex molecules. Entropy increases when a system is heated and when solutions form. Using these guidelines, the sign of entropy changes for some chemical reactions and physical changes may be reliably predicted.

Key Equations

- $\Delta S = \frac{q_{\text{rev}}}{T}$
- $S = k \ln W$
- $\Delta S = k \ln \frac{W_f}{W_i}$

Chemistry End of Chapter Exercises

Exercise:

Problem:

In [\[link\]](#) all possible distributions and microstates are shown for four different particles shared between two boxes. Determine the entropy change, ΔS , if the particles are initially evenly distributed between the two boxes, but upon redistribution all end up in Box (b).

Exercise:

Problem:

In [\[link\]](#) all of the possible distributions and microstates are shown for four different particles shared between two boxes. Determine the entropy change, ΔS , for the system when it is converted from distribution (b) to distribution (d).

Solution:

There are four initial microstates and four final microstates.

$$\Delta S = k \ln \frac{W_f}{W_i} = 1.38 \times 10^{-23} \text{ J/K} \times \ln \frac{4}{4} = 0$$

Exercise:**Problem:**

How does the process described in the previous item relate to the system shown in [\[link\]](#)?

Exercise:**Problem:**

Consider a system similar to the one in [\[link\]](#), except that it contains six particles instead of four. What is the probability of having all the particles in only one of the two boxes in the case? Compare this with the similar probability for the system of four particles that we have derived to be equal to $\frac{1}{8}$. What does this comparison tell us about even larger systems?

Solution:

The probability for all the particles to be on one side is $\frac{1}{32}$. This probability is noticeably lower than the $\frac{1}{8}$ result for the four-particle system. The conclusion we can make is that the probability for all the particles to stay in only one part of the system will decrease rapidly as the number of particles increases, and, for instance, the probability for all molecules of gas to gather in only one side of a room at room temperature and pressure is negligible since the number of gas molecules in the room is very large.

Exercise:**Problem:**

Consider the system shown in [\[link\]](#). What is the change in entropy for the process where the energy is initially associated only with particle A, but in the final state the energy is distributed between two different particles?

Exercise:**Problem:**

Consider the system shown in [\[link\]](#). What is the change in entropy for the process where the energy is initially associated with particles A and B, and the energy is distributed between two particles in different boxes (one in A-B, the other in C-D)?

Solution:

There is only one initial state. For the final state, the energy can be contained in pairs A-C, A-D, B-C, or B-D. Thus, there are four final possible states.

$$\Delta S = k \ln \left(\frac{W_f}{W_i} \right) = 1.38 \times 10^{-23} \text{ J/K} \times \ln \left(\frac{4}{1} \right) = 1.91 \times 10^{-23} \text{ J/K}$$

Exercise:**Problem:**

Arrange the following sets of systems in order of increasing entropy. Assume one mole of each substance and the same temperature for each member of a set.

(a) $\text{H}_2(g)$, $\text{HBrO}_4(g)$, $\text{HBr}(g)$

(b) $\text{H}_2\text{O}(l)$, $\text{H}_2\text{O}(g)$, $\text{H}_2\text{O}(s)$

(c) $\text{He}(g)$, $\text{Cl}_2(g)$, $\text{P}_4(g)$

Exercise:

Problem:

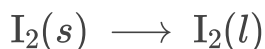
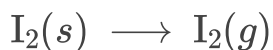
At room temperature, the entropy of the halogens increases from I_2 to Br_2 to Cl_2 . Explain.

Solution:

The masses of these molecules would suggest the opposite trend in their entropies. The observed trend is a result of the more significant variation of entropy with a physical state. At room temperature, I_2 is a solid, Br_2 is a liquid, and Cl_2 is a gas.

Exercise:**Problem:**

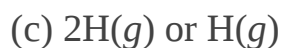
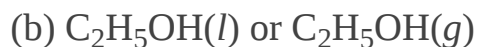
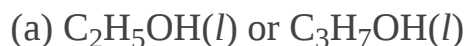
Consider two processes: sublimation of $\text{I}_2(s)$ and melting of $\text{I}_2(s)$ (Note: the latter process can occur at the same temperature but somewhat higher pressure).



Is ΔS positive or negative in these processes? In which of the processes will the magnitude of the entropy change be greater?

Exercise:**Problem:**

Indicate which substance in the given pairs has the higher entropy value. Explain your choices.

**Solution:**

(a) $\text{C}_3\text{H}_7\text{OH}(l)$ as it is a larger molecule (more complex and more massive), and so more microstates describing its motions are available at any given temperature. (b) $\text{C}_2\text{H}_5\text{OH}(g)$ as it is in the gaseous state. (c) $2\text{H}(g)$, since entropy is an extensive property, and so two H atoms (or two moles of H atoms) possess twice as much entropy as one atom (or one mole of atoms).

Exercise:

Problem:

Predict the sign of the entropy change for the following processes.

- (a) An ice cube is warmed to near its melting point.
- (b) Exhaled breath forms fog on a cold morning.
- (c) Snow melts.

Exercise:

Problem:

Predict the sign of the entropy change for the following processes. Give a reason for your prediction.

- (a) $\text{Pb}^{2+}(aq) + \text{S}^{2-}(aq) \longrightarrow \text{PbS}(s)$
- (b) $2\text{Fe}(s) + \frac{3}{2}\text{O}_2(g) \longrightarrow \text{Fe}_2\text{O}_3(s)$
- (c) $2\text{C}_6\text{H}_{14}(l) + 19\text{O}_2(g) \longrightarrow 14\text{H}_2\text{O}(g) + 12\text{CO}_2(g)$

Solution:

(a) Negative. The relatively ordered solid precipitating decreases the number of mobile ions in solution. (b) Negative. There is a net loss of three moles of gas from reactants to products. (c) Positive. There is a net increase of seven moles of gas from reactants to products.

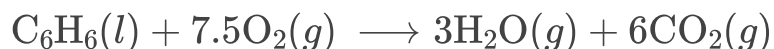
Exercise:

Problem:

Write the balanced chemical equation for the combustion of methane, $\text{CH}_4(g)$, to give carbon dioxide and water vapor. Explain why it is difficult to predict whether ΔS is positive or negative for this chemical reaction.

Exercise:**Problem:**

Write the balanced chemical equation for the combustion of benzene, $\text{C}_6\text{H}_6(l)$, to give carbon dioxide and water vapor. Would you expect ΔS to be positive or negative in this process?

Solution:

There are 7.5 moles of gas initially, and $3 + 6 = 9$ moles of gas in the end. Therefore, it is likely that the entropy increases as a result of this reaction, and ΔS is positive.

Glossaryentropy (S)

state function that is a measure of the matter and/or energy dispersal within a system, determined by the number of system microstates often described as a measure of the disorder of the system

microstate (W)

possible configuration or arrangement of matter and energy within a system

reversible process

process that takes place so slowly as to be capable of reversing direction in response to an infinitesimally small change in conditions; hypothetical construct that can only be approximated by real processes removed

The Second and Third Laws of Thermodynamics

By the end of this section, you will be able to:

- State and explain the second and third laws of thermodynamics
- Calculate entropy changes for phase transitions and chemical reactions under standard conditions

The Second Law of Thermodynamics

In the quest to identify a property that may reliably predict the spontaneity of a process, we have identified a very promising candidate: entropy. Processes that involve an increase in entropy *of the system* ($\Delta S > 0$) are very often spontaneous; however, examples to the contrary are plentiful. By expanding consideration of entropy changes to include *the surroundings*, we may reach a significant conclusion regarding the relation between this property and spontaneity. In thermodynamic models, the system and surroundings comprise everything, that is, the universe, and so the following is true:

Equation:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

To illustrate this relation, consider again the process of heat flow between two objects, one identified as the system and the other as the surroundings. There are three possibilities for such a process:

1. The objects are at different temperatures, and heat flows from the hotter to the cooler object. *This is always observed to occur spontaneously.* Designating the hotter object as the system and invoking the definition of entropy yields the following:

Equation:

$$\Delta S_{\text{sys}} = \frac{-q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T_{\text{surr}}}$$

The arithmetic signs of q_{rev} denote the loss of heat by the system and the gain of heat by the surroundings. Since $T_{\text{sys}} > T_{\text{surr}}$ in this scenario, the magnitude of the entropy change for the surroundings will be greater than that for the system, and so the sum of ΔS_{sys} and ΔS_{surr} will yield a positive value for ΔS_{univ} . *This process involves an increase in the entropy of the universe.*

2. The objects are at different temperatures, and heat flows from the cooler to the hotter object. *This is never observed to occur spontaneously.* Again designating the hotter object as the system and invoking the definition of entropy yields the following:

Equation:

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{-q_{\text{rev}}}{T_{\text{surr}}}$$

The arithmetic signs of q_{rev} denote the gain of heat by the system and the loss of heat by the surroundings. The magnitude of the entropy change for the surroundings will again be greater than that for the system, but in this case, the signs of the heat changes will yield a negative value for ΔS_{univ} . *This process involves a decrease in the entropy of the universe.*

3. The temperature difference between the objects is infinitesimally small, $T_{\text{sys}} \approx T_{\text{surr}}$, and so the heat flow is thermodynamically reversible. See the previous section's discussion). In this case, the system and surroundings experience entropy changes that are equal in magnitude and therefore sum to yield a value of zero for ΔS_{univ} . *This process involves no change in the entropy of the universe.*

These results lead to a profound statement regarding the relation between entropy and spontaneity known as the **second law of thermodynamics**: *all spontaneous changes cause an increase in the entropy of the universe*. A summary of these three relations is provided in [\[link\]](#).

The Second Law of Thermodynamics	
$\Delta S_{\text{univ}} > 0$	spontaneous
$\Delta S_{\text{univ}} < 0$	nonspontaneous (spontaneous in opposite direction)
$\Delta S_{\text{univ}} = 0$	reversible (system is at equilibrium)

For many realistic applications, the surroundings are vast in comparison to the system. In such cases, the heat gained or lost by the surroundings as a result of some process represents a very small, nearly infinitesimal, fraction of its total thermal energy. For example, combustion of a fuel in air involves transfer of heat from a system (the fuel and oxygen molecules undergoing reaction) to surroundings that are infinitely more massive (the earth's atmosphere). As a result, q_{surr} is a good approximation of q_{rev} , and the second law may be stated as the following:

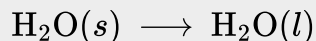
Equation:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T}$$

We may use this equation to predict the spontaneity of a process as illustrated in [\[link\]](#).

Example:**Will Ice Spontaneously Melt?**

The entropy change for the process

Equation:

is 22.1 J/K and requires that the surroundings transfer 6.00 kJ of heat to the system. Is the process spontaneous at $-10.00\text{ }^\circ\text{C}$? Is it spontaneous at $+10.00\text{ }^\circ\text{C}$?

Solution

We can assess the spontaneity of the process by calculating the entropy change of the universe. If ΔS_{univ} is positive, then the process is spontaneous. At both temperatures, $\Delta S_{\text{sys}} = 22.1\text{ J/K}$ and $q_{\text{surr}} = -6.00\text{ kJ}$.

At $-10.00\text{ }^\circ\text{C}$ (263.15 K), the following is true:

Equation:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \\ &= 22.1\text{ J/K} + \frac{-6.00 \times 10^3\text{ J}}{263.15\text{ K}} = -0.7\text{ J/K}\end{aligned}$$

$S_{\text{univ}} < 0$, so melting is nonspontaneous (*not* spontaneous) at $-10.0\text{ }^\circ\text{C}$.

At $10.00\text{ }^\circ\text{C}$ (283.15 K), the following is true:

Equation:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \\ &= 22.1\text{ J/K} + \frac{-6.00 \times 10^3\text{ J}}{283.15\text{ K}} = +0.9\text{ J/K}\end{aligned}$$

$S_{\text{univ}} > 0$, so melting *is* spontaneous at $10.00\text{ }^\circ\text{C}$.

Check Your Learning

Using this information, determine if liquid water will spontaneously freeze at the same temperatures. What can you say about the values of S_{univ} ?

Note:**Answer:**

Entropy is a state function, and freezing is the opposite of melting. At $-10.00\text{ }^\circ\text{C}$ spontaneous, $+0.7\text{ J/K}$; at $+10.00\text{ }^\circ\text{C}$ nonspontaneous, -0.9 J/K .

The Third Law of Thermodynamics

The previous section described the various contributions of matter and energy dispersal that contribute to the entropy of a system. With these contributions in mind, consider the entropy of a pure, perfectly crystalline solid possessing no kinetic energy (that is, at a temperature of absolute zero, 0 K). This system may be described by a single microstate, as its purity, perfect crystallinity and complete lack of motion means there is but one possible location for each identical atom or molecule comprising the crystal ($W = 1$). According to the Boltzmann equation, the entropy of this system is zero.

Equation:

$$S = k \ln W = k \ln(1) = 0$$

This limiting condition for a system's entropy represents the **third law of thermodynamics**: *the entropy of a pure, perfect crystalline substance at 0 K is zero.*

We can make careful calorimetric measurements to determine the temperature dependence of a substance's entropy and to derive absolute entropy values under specific conditions.

Standard entropies are given the label S_{298}° for values determined for one mole of substance at a pressure of 1 bar and a temperature of 298 K. The **standard entropy change** (ΔS°) for any process may be computed from the standard entropies of its reactant and product species like the following:

Equation:

$$\Delta S^\circ = \sum \nu S_{298}^\circ(\text{products}) - \sum \nu S_{298}^\circ(\text{reactants})$$

Here, ν represents stoichiometric coefficients in the balanced equation representing the process. For example, ΔS° for the following reaction at room temperature

Equation:



is computed as the following:

Equation:

$$= \left[xS_{298}^\circ(C) + yS_{298}^\circ(D) \right] - \left[mS_{298}^\circ(A) + nS_{298}^\circ(B) \right]$$

[\[link\]](#) lists some standard entropies at 298.15 K. You can find additional standard entropies in [Appendix G](#).

Standard Entropies (at 298.15 K, 1 atm)	
Substance	S_{298}° (J mol ⁻¹ K ⁻¹)
carbon	
C(s, graphite)	5.740
C(s, diamond)	2.38
CO(<i>g</i>)	197.7
CO ₂ (<i>g</i>)	213.8
CH ₄ (<i>g</i>)	186.3
C ₂ H ₄ (<i>g</i>)	219.5
C ₂ H ₆ (<i>g</i>)	229.5
CH ₃ OH(<i>l</i>)	126.8
C ₂ H ₅ OH(<i>l</i>)	160.7
hydrogen	
H ₂ (<i>g</i>)	130.57
H(<i>g</i>)	114.6
H ₂ O(<i>g</i>)	188.71
H ₂ O(<i>l</i>)	69.91
HCl(<i>g</i>)	186.8
H ₂ S(<i>g</i>)	205.7
oxygen	
O ₂ (<i>g</i>)	205.03

Example:**Determination of ΔS°**

Calculate the standard entropy change for the following process:

Equation:**Solution**

The value of the standard entropy change at room temperature, ΔS_{298}° , is the difference between the standard entropy of the product, $\text{H}_2\text{O}(l)$, and the standard entropy of the reactant, $\text{H}_2\text{O}(g)$.

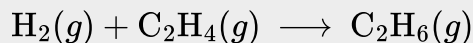
Equation:

$$\begin{aligned}\Delta S_{298}^\circ &= S_{298}^\circ(\text{H}_2\text{O}(l)) - S_{298}^\circ(\text{H}_2\text{O}(g)) \\ &= (70.0 \text{ J mol}^{-1} \text{ K}^{-1}) - (188.8 \text{ J mol}^{-1} \text{ K}^{-1}) = -118.8 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

The value for ΔS_{298}° is negative, as expected for this phase transition (condensation), which the previous section discussed.

Check Your Learning

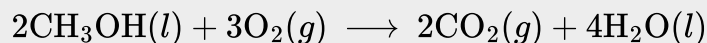
Calculate the standard entropy change for the following process:

Equation:**Note:****Answer:**

$$-120.6 \text{ J mol}^{-1} \text{ K}^{-1}$$

Example:**Determination of ΔS°**

Calculate the standard entropy change for the combustion of methanol, CH_3OH :

Equation:**Solution**

The value of the standard entropy change is equal to the difference between the standard entropies of the products and the entropies of the reactants scaled by their stoichiometric coefficients.

Equation:

$$\Delta S^{\circ} = \Delta S_{298}^{\circ} = \sum \nu S_{298}^{\circ}(\text{products}) - \sum \nu S_{298}^{\circ}(\text{reactants})$$

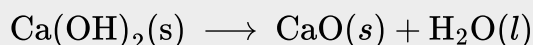
Equation:

$$\begin{aligned} & [2S_{298}^{\circ}(\text{CO}_2(g)) + 4S_{298}^{\circ}(\text{H}_2\text{O}(l))] - [2S_{298}^{\circ}(\text{CH}_3\text{OH}(l)) + 3S_{298}^{\circ}(\text{O}_2(g))] \\ & = \{ [2(213.8) + 4 \times 70.0] - [2(126.8) + 3(205.03)] \} = -161.1 \text{ J/mol}\cdot\text{K} \end{aligned}$$

Check Your Learning

Calculate the standard entropy change for the following reaction:

Equation:



Note:

Answer:

24.7 J/mol·K

Key Concepts and Summary

The second law of thermodynamics states that a spontaneous process increases the entropy of the universe, $S_{\text{univ}} > 0$. If $\Delta S_{\text{univ}} < 0$, the process is nonspontaneous, and if $\Delta S_{\text{univ}} = 0$, the system is at equilibrium. The third law of thermodynamics establishes the zero for entropy as that of a perfect, pure crystalline solid at 0 K. With only one possible microstate, the entropy is zero. We may compute the standard entropy change for a process by using standard entropy values for the reactants and products involved in the process.

Key Equations

- $\Delta S^{\circ} = \Delta S_{298}^{\circ} = \sum \nu S_{298}^{\circ}(\text{products}) - \sum \nu S_{298}^{\circ}(\text{reactants})$
- $\Delta S = \frac{q_{\text{rev}}}{T}$
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$

- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T}$

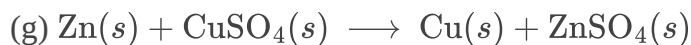
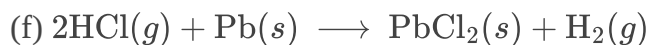
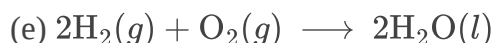
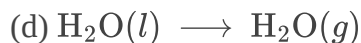
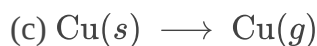
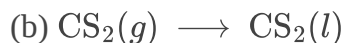
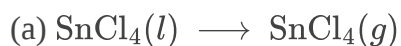
Chemistry End of Chapter Exercises

Exercise:

Problem: What is the difference between ΔS , ΔS° , and ΔS_{298}° for a chemical change?

Exercise:

Problem: Calculate ΔS_{298}° for the following changes.



Solution:

(a) 107 J/K; (b) -86.4 J/K; (c) 133.2 J/K; (d) 118.8 J/K; (e) -326.6 J/K; (f) -171.9 J/K; (g) -7.2 J/K

Exercise:

Problem:

Determine the entropy change for the combustion of liquid ethanol, $\text{C}_2\text{H}_5\text{OH}$, under the standard conditions to give gaseous carbon dioxide and liquid water.

Exercise:

Problem:

Determine the entropy change for the combustion of gaseous propane, C_3H_8 , under the standard conditions to give gaseous carbon dioxide and water.

Solution:

100.6 J/K

Exercise:

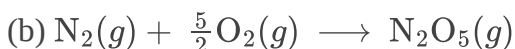
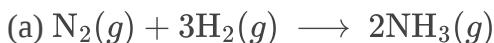
Problem:

“Thermite” reactions have been used for welding metal parts such as railway rails and in metal refining. One such thermite reaction is $\text{Fe}_2\text{O}_3(s) + 2\text{Al}(s) \longrightarrow \text{Al}_2\text{O}_3(s) + 2\text{Fe}(s)$. Is the reaction spontaneous at room temperature under standard conditions? During the reaction, the surroundings absorb 851.8 kJ/mol of heat.

Exercise:

Problem:

Using the relevant S_{298}° values listed in [Appendix G](#), calculate ΔS_{298}° for the following changes:

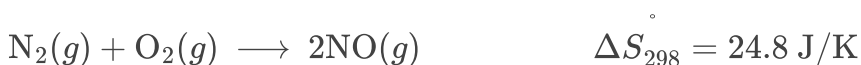
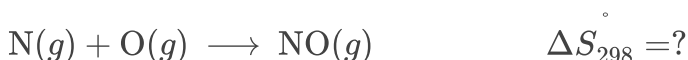


Solution:

(a) -198.1 J/K ; (b) -348.9 J/K

Exercise:

Problem: From the following information, determine ΔS_{298}° for the following:



Exercise:

Problem:

By calculating ΔS_{univ} at each temperature, determine if the melting of 1 mole of $\text{NaCl}(s)$ is spontaneous at 500°C and at 700°C .

$$S_{\text{NaCl}(s)} = 72.11 \frac{\text{J}}{\text{mol}\cdot\text{K}} \quad S_{\text{NaCl}(l)} = 95.06 \frac{\text{J}}{\text{mol}\cdot\text{K}} \quad \Delta H_{\text{fusion}}^\circ = 27.95 \text{ kJ/mol}$$

What assumptions are made about the thermodynamic information (entropy and enthalpy values) used to solve this problem?

Solution:

As $\Delta S_{\text{univ}} < 0$ at each of these temperatures, melting is not spontaneous at either of them. The given values for entropy and enthalpy are for NaCl at 298 K. It is assumed that these do not change significantly at the higher temperatures used in the problem.

Exercise:

Problem:

Use the standard entropy data in [Appendix G](#) to determine the change in entropy for each of the reactions listed in [\[link\]](#). All the processes occur at the standard conditions and 25 °C.

Exercise:

Problem:

Use the standard entropy data in [Appendix G](#) to determine the change in entropy for each of the reactions listed in [\[link\]](#). All the processes occur at the standard conditions and 25 °C.

Solution:

(a) 2.86 J/K; (b) 24.8 J/K; (c) -113.2 J/K; (d) -24.7 J/K; (e) 15.5 J/K; (f) 290.0 J/K

Glossary

second law of thermodynamics

entropy of the universe increases for a spontaneous process

standard entropy (S°)

entropy for a substance at 1 bar pressure; tabulated values are usually determined at 298.15 K and denoted S_{298}°

standard entropy change (ΔS°)

change in entropy for a reaction calculated using the standard entropies, usually at room temperature and denoted ΔS_{298}°

third law of thermodynamics

entropy of a perfect crystal at absolute zero (0 K) is zero

Free Energy

By the end of this section, you will be able to:

- Define Gibbs free energy, and describe its relation to spontaneity
- Calculate free energy change for a process using free energies of formation for its reactants and products
- Calculate free energy change for a process using enthalpies of formation and the entropies for its reactants and products
- Explain how temperature affects the spontaneity of some processes
- Relate standard free energy changes to equilibrium constants

One of the challenges of using the second law of thermodynamics to determine if a process is spontaneous is that we must determine the entropy change for the system *and* the entropy change for the surroundings. An alternative approach involving a new thermodynamic property defined in terms of system properties only was introduced in the late nineteenth century by American mathematician Josiah Willard Gibbs. This new property is called the **Gibbs free energy change (G)** (or simply the *free energy*), and it is defined in terms of a system's enthalpy and entropy as the following:

Equation:

$$G = H - TS$$

Free energy is a state function, and at constant temperature and pressure, the **standard free energy change (ΔG°)** may be expressed as the following:

Equation:

$$\Delta G = \Delta H - T\Delta S$$

(For simplicity's sake, the subscript "sys" will be omitted henceforth.)

We can understand the relationship between this system property and the spontaneity of a process by recalling the previously derived second law expression:

Equation:

$$\Delta S_{\text{univ}} = \Delta S + \frac{q_{\text{surr}}}{T}$$

The first law requires that $q_{\text{surr}} = -q_{\text{sys}}$, and at constant pressure $q_{\text{sys}} = \Delta H$, and so this expression may be rewritten as the following:

Equation:

$$\Delta S_{\text{univ}} = \Delta S - \frac{\Delta H}{T}$$

ΔH is the enthalpy change *of the system*. Multiplying both sides of this equation by $-T$, and rearranging yields the following:

Equation:

$$-T\Delta S_{\text{univ}} = \Delta H - T\Delta S$$

Comparing this equation to the previous one for free energy change shows the following relation:

Equation:

$$\Delta G = -T\Delta S_{\text{univ}}$$

The free energy change is therefore a reliable indicator of the spontaneity of a process, being directly related to the previously identified spontaneity indicator, ΔS_{univ} . [\[link\]](#) summarizes the relation between the spontaneity of a process and the arithmetic signs of these indicators.

Relation between Process Spontaneity and Signs of Thermodynamic Properties		
$\Delta S_{\text{univ}} > 0$	$\Delta G < 0$	spontaneous
$\Delta S_{\text{univ}} < 0$	$\Delta G > 0$	nonspontaneous
$\Delta S_{\text{univ}} = 0$	$\Delta G = 0$	reversible (at equilibrium)

Calculating Free Energy Change

Free energy is a state function, so its value depends only on the conditions of the initial and final states of the system. A convenient and common approach to the calculation of free energy changes for physical and chemical reactions is by use of widely available compilations of standard state thermodynamic data. One method involves the use of standard enthalpies and entropies to compute standard free energy changes according to the following relation as demonstrated in [\[link\]](#).

Equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Example:

Evaluation of ΔG° from ΔH° and ΔS°

Use standard enthalpy and entropy data from [Appendix G](#) to calculate the standard free energy change for the vaporization of water at room temperature (298 K). What does the computed value for ΔG° say about the spontaneity of this process?

Solution

The process of interest is the following:

Equation:

$$\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g)$$

The standard change in free energy may be calculated using the following equation:

Equation:

$$\Delta G_{298}^\circ = \Delta H^\circ - T\Delta S^\circ$$

From [Appendix G](#), here is the data:

Substance	ΔH_f° (kJ/mol)	S_{298}° (J/K·mol)

Substance	ΔH_f° (kJ/mol)	S_{298}° (J/K·mol)
H ₂ O(l)	-286.83	70.0
H ₂ O(g)	-241.82	188.8

Combining at 298 K:

Equation:

$$\begin{aligned}\Delta H^\circ &= \Delta H_{298}^\circ = \Delta H_f^\circ (\text{H}_2\text{O}(g)) - \Delta H_f^\circ (\text{H}_2\text{O}(l)) \\ &= [-241.82 \text{ kJ} - (-286.83)] \text{ kJ/mol} = 44.01 \text{ kJ/mol}\end{aligned}$$

Equation:

$$\begin{aligned}\Delta S^\circ &= \Delta S_{298}^\circ = S_{298}^\circ (\text{H}_2\text{O}(g)) - S_{298}^\circ (\text{H}_2\text{O}(l)) \\ &= 188.8 \text{ J/mol}\cdot\text{K} - 70.0 \text{ J/K} = 118.8 \text{ J/mol}\cdot\text{K}\end{aligned}$$

Equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Converting everything into kJ and combining at 298 K:

Equation:

$$\begin{aligned}\Delta G_{298}^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= 44.01 \text{ kJ/mol} - (298 \text{ K} \times 118.8 \text{ J/mol}\cdot\text{K}) \times \frac{1 \text{ kJ}}{1000 \text{ J}}\end{aligned}$$

Equation:

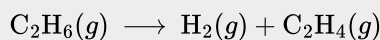
$$44.01 \text{ kJ/mol} - 35.4 \text{ kJ/mol} = 9.6 \text{ kJ/mol}$$

At 298 K (25 °C) $\Delta G_{298}^\circ > 0$, and so boiling is nonspontaneous (*not* spontaneous).

Check Your Learning

Use standard enthalpy and entropy data from [Appendix G](#) to calculate the standard free energy change for the reaction shown here (298 K). What does the computed value for ΔG° say about the spontaneity of this process?

Equation:



Note:

Answer:

$\Delta G_{298}^\circ = 102.0 \text{ kJ/mol}$; the reaction is nonspontaneous (*not* spontaneous) at 25 °C.

The standard free energy change for a reaction may also be calculated from **standard free energy of formation** (ΔG_f°), values of the reactants and products involved in the reaction. The standard free energy of formation is the

free energy change that accompanies the formation of one mole of a substance from its elements in their standard states. Similar to the standard enthalpy of formation, ΔG_f° is by definition zero for elemental substances under standard state conditions. The approach used to calculate ΔG° for a reaction from ΔG_f° values is the same as that demonstrated previously for enthalpy and entropy changes. For the reaction

Equation:



the standard free energy change at room temperature may be calculated as

Equation:

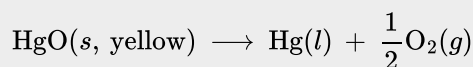
$$\begin{aligned}\Delta G_{298}^\circ &= \Delta G^\circ = \sum \nu \Delta G_{298}^\circ(\text{products}) - \sum \nu \Delta G_{298}^\circ(\text{reactants}) \\ &= [x\Delta G_f^\circ(\text{C}) + y\Delta G_f^\circ(\text{D})] - [m\Delta G_f^\circ(\text{A}) + n\Delta G_f^\circ(\text{B})].\end{aligned}$$

Example:

Calculation of ΔG_{298}°

Consider the decomposition of yellow mercury(II) oxide.

Equation:



Calculate the standard free energy change at room temperature, ΔG_{298}° , using (a) standard free energies of formation and (b) standard enthalpies of formation and standard entropies. Do the results indicate the reaction to be spontaneous or nonspontaneous under standard conditions?

Solution

The required data are available in [Appendix G](#) and are shown here.

Compound	ΔG_f° (kJ/mol)	ΔH_f° (kJ/mol)	S_{298}° (J/K·mol)
HgO (s, yellow)	-58.43	-90.46	71.13
Hg(l)	0	0	75.9
O ₂ (g)	0	0	205.2

(a) Using free energies of formation:

Equation:

$$\Delta G_{298}^\circ = \sum \nu \Delta G_f^\circ(\text{products}) - \sum \nu \Delta G_f^\circ(\text{reactants})$$

Equation:

$$= \left[1\Delta G_f^\circ \text{Hg}(l) + \frac{1}{2}\Delta G_f^\circ \text{O}_2(g) \right] - 1\Delta G_f^\circ \text{HgO}(s, \text{yellow})$$

Equation:

$$= \left[1 \text{ mol}(0 \text{ kJ/mol}) + \frac{1}{2} \text{ mol}(0 \text{ kJ/mol}) \right] - 1 \text{ mol}(-58.43 \text{ kJ/mol}) = 58.43 \text{ kJ/mol}$$

(b) Using enthalpies and entropies of formation:

Equation:

$$\Delta H_{298}^\circ = \sum \nu \Delta H_f^\circ (\text{products}) - \sum \nu \Delta H_f^\circ (\text{reactants})$$

Equation:

$$= \left[1\Delta H_f^\circ \text{Hg}(l) + \frac{1}{2}\Delta H_f^\circ \text{O}_2(g) \right] - 1\Delta H_f^\circ \text{HgO}(s, \text{yellow})$$

Equation:

$$= \left[1 \text{ mol}(0 \text{ kJ/mol}) + \frac{1}{2} \text{ mol}(0 \text{ kJ/mol}) \right] - 1 \text{ mol}(-90.46 \text{ kJ/mol}) = 90.46 \text{ kJ/mol}$$

Equation:

$$\Delta S_{298}^\circ = \sum \nu \Delta S_{298}^\circ (\text{products}) - \sum \nu \Delta S_{298}^\circ (\text{reactants})$$

Equation:

$$= \left[1\Delta S_{298}^\circ \text{Hg}(l) + \frac{1}{2}\Delta S_{298}^\circ \text{O}_2(g) \right] - 1\Delta S_{298}^\circ \text{HgO}(s, \text{yellow})$$

Equation:

$$= \left[1 \text{ mol}(75.9 \text{ J/mol K}) + \frac{1}{2} \text{ mol}(205.2 \text{ J/mol K}) \right] - 1 \text{ mol}(71.13 \text{ J/mol K}) = 107.4 \text{ J/mol K}$$

Equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 90.46 \text{ kJ} - 298.15 \text{ K} \times 107.4 \text{ J/K}\cdot\text{mol} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

Equation:

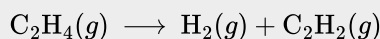
$$\Delta G^\circ = (90.46 - 32.01) \text{ kJ/mol} = 58.45 \text{ kJ/mol}$$

Both ways to calculate the standard free energy change at 25 °C give the same numerical value (to three significant figures), and both predict that the process is nonspontaneous (*not* spontaneous) at room temperature.

Check Your Learning

Calculate ΔG° using (a) free energies of formation and (b) enthalpies of formation and entropies ([Appendix G](#)). Do the results indicate the reaction to be spontaneous or nonspontaneous at 25 °C?

Equation:



Note:

Answer:

(a) 140.8 kJ/mol, nonspontaneous

(b) 141.5 kJ/mol, nonspontaneous

Temperature Dependence of Spontaneity

As was previously demonstrated in this chapter's section on entropy, the spontaneity of a process may depend upon the temperature of the system. Phase transitions, for example, will proceed spontaneously in one direction or the other depending upon the temperature of the substance in question. Likewise, some chemical reactions can also exhibit temperature dependent spontaneities. To illustrate this concept, the equation relating free energy change to the enthalpy and entropy changes for the process is considered:

Equation:

$$\Delta G = \Delta H - T\Delta S$$

The spontaneity of a process, as reflected in the arithmetic sign of its free energy change, is then determined by the signs of the enthalpy and entropy changes and, in some cases, the absolute temperature. Since T is the absolute (kelvin) temperature, it can only have positive values. Four possibilities therefore exist with regard to the signs of the enthalpy and entropy changes:

1. **Both ΔH and ΔS are positive.** This condition describes an endothermic process that involves an increase in system entropy. In this case, ΔG will be negative if the magnitude of the $T\Delta S$ term is greater than ΔH . If the $T\Delta S$ term is less than ΔH , the free energy change will be positive. Such a process is *spontaneous at high temperatures and nonspontaneous at low temperatures*.
2. **Both ΔH and ΔS are negative.** This condition describes an exothermic process that involves a decrease in system entropy. In this case, ΔG will be negative if the magnitude of the $T\Delta S$ term is less than ΔH . If the $T\Delta S$ term's magnitude is greater than ΔH , the free energy change will be positive. Such a process is *spontaneous at low temperatures and nonspontaneous at high temperatures*.
3. **ΔH is positive and ΔS is negative.** This condition describes an endothermic process that involves a decrease in system entropy. In this case, ΔG will be positive regardless of the temperature. Such a process is *nonspontaneous at all temperatures*.
4. **ΔH is negative and ΔS is positive.** This condition describes an exothermic process that involves an increase in system entropy. In this case, ΔG will be negative regardless of the temperature. Such a process is *spontaneous at all temperatures*.

These four scenarios are summarized in [\[link\]](#).

Summary of the Four Scenarios for Enthalpy and Entropy Changes

	$\Delta H > 0$ (endothermic)	$\Delta H < 0$ (exothermic)
$\Delta S > 0$ (increase in entropy)	$\Delta G < 0$ at high temperature $\Delta G > 0$ at low temperature Process is spontaneous at high temperature	$\Delta G < 0$ at any temperature Process is spontaneous at any temperature
$\Delta S < 0$ (decrease in entropy)	$\Delta G > 0$ at any temperature Process is nonspontaneous at any temperature	$\Delta G < 0$ at low temperature $\Delta G > 0$ at high temperature Process is spontaneous at low temperature

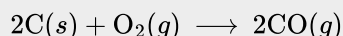
There are four possibilities regarding the signs of enthalpy and entropy changes.

Example:

Predicting the Temperature Dependence of Spontaneity

The incomplete combustion of carbon is described by the following equation:

Equation:



How does the spontaneity of this process depend upon temperature?

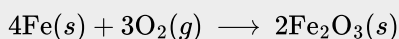
Solution

Combustion processes are exothermic ($\Delta H < 0$). This particular reaction involves an increase in entropy due to the accompanying increase in the amount of gaseous species (net gain of one mole of gas, $\Delta S > 0$). The reaction is therefore spontaneous ($\Delta G < 0$) at all temperatures.

Check Your Learning

Popular chemical hand warmers generate heat by the air-oxidation of iron:

Equation:



How does the spontaneity of this process depend upon temperature?

Note:

Answer:

ΔH and ΔS are negative; the reaction is spontaneous at low temperatures.

When considering the conclusions drawn regarding the temperature dependence of spontaneity, it is important to keep in mind what the terms “high” and “low” mean. Since these terms are adjectives, the temperatures in question are deemed high or low relative to some reference temperature. A process that is nonspontaneous at one temperature but spontaneous at another will necessarily undergo a change in “spontaneity” (as reflected by its ΔG).

as temperature varies. This is clearly illustrated by a graphical presentation of the free energy change equation, in which ΔG is plotted on the y axis versus T on the x axis:

Equation:

$$\Delta G = \Delta H - T\Delta S$$

Equation:

$$y = b + mx$$

Such a plot is shown in [\[link\]](#). A process whose enthalpy and entropy changes are of the same arithmetic sign will exhibit a temperature-dependent spontaneity as depicted by the two yellow lines in the plot. Each line crosses from one spontaneity domain (positive or negative ΔG) to the other at a temperature that is characteristic of the process in question. This temperature is represented by the x-intercept of the line, that is, the value of T for which ΔG is zero:

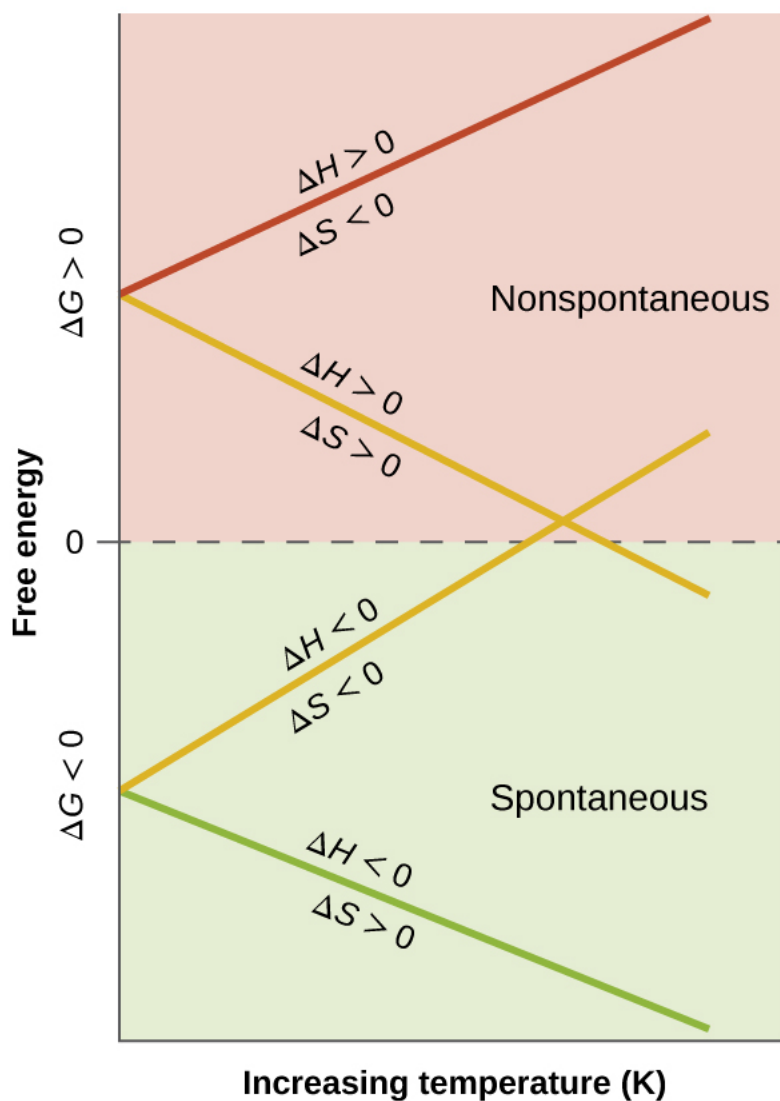
Equation:

$$\Delta G = 0 = \Delta H - T\Delta S$$

Equation:

$$T = \frac{\Delta H}{\Delta S}$$

And so, saying a process is spontaneous at “high” or “low” temperatures means the temperature is above or below, respectively, that temperature at which ΔG for the process is zero. As noted earlier, the condition of $\Delta G = 0$ describes a system at equilibrium.



These plots show the variation in ΔG with temperature for the four possible combinations of arithmetic sign for ΔH and ΔS .

Example:

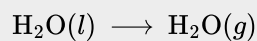
Equilibrium Temperature for a Phase Transition

As defined in the chapter on liquids and solids, the boiling point of a liquid is the temperature at which its liquid and gaseous phases are in equilibrium (that is, when vaporization and condensation occur at equal rates). Use the information in [Appendix G](#) to estimate the boiling point of water.

Solution

The process of interest is the following phase change:

Equation:



When this process is at equilibrium, $\Delta G = 0$, so the following is true:

Equation:

$$0 = \Delta H^\circ - T\Delta S^\circ \quad \text{or} \quad T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

Using the standard thermodynamic data from [Appendix G](#),

Equation:

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ(\text{H}_2\text{O}(g)) - \Delta H_f^\circ(\text{H}_2\text{O}(l)) \\ &= -241.82 \text{ kJ/mol} - (-286.83 \text{ kJ/mol}) = 44.01 \text{ kJ/mol}\end{aligned}$$

Equation:

$$\begin{aligned}\Delta S^\circ &= \Delta S_{298}^\circ(\text{H}_2\text{O}(g)) - \Delta S_{298}^\circ(\text{H}_2\text{O}(l)) \\ &= 188.8 \text{ J/K}\cdot\text{mol} - 70.0 \text{ J/K}\cdot\text{mol} = 118.8 \text{ J/K}\cdot\text{mol}\end{aligned}$$

Equation:

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{44.01 \times 10^3 \text{ J/mol}}{118.8 \text{ J/K}\cdot\text{mol}} = 370.5 \text{ K} = 97.3^\circ\text{C}$$

The accepted value for water's normal boiling point is 373.2 K (100.0 °C), and so this calculation is in reasonable agreement. Note that the values for enthalpy and entropy changes data used were derived from standard data at 298 K ([Appendix G](#)). If desired, you could obtain more accurate results by using enthalpy and entropy changes determined at (or at least closer to) the actual boiling point.

Check Your Learning

Use the information in [Appendix G](#) to estimate the boiling point of CS₂.

Note:

Answer:

313 K (accepted value 319 K)

Free Energy and Equilibrium

The free energy change for a process may be viewed as a measure of its driving force. A negative value for ΔG represents a finite driving force for the process in the forward direction, while a positive value represents a driving force for the process in the reverse direction. When ΔG is zero, the forward and reverse driving forces are equal, and so the process occurs in both directions at the same rate (the system is at equilibrium).

In the chapter on equilibrium the *reaction quotient*, Q , was introduced as a convenient measure of the status of an equilibrium system. Recall that Q is the numerical value of the mass action expression for the system, and that you may use its value to identify the direction in which a reaction will proceed in order to achieve equilibrium. When Q is lesser than the equilibrium constant, K , the reaction will proceed in the forward direction until equilibrium is reached and $Q = K$. Conversely, if $Q > K$, the process will proceed in the reverse direction until equilibrium is achieved.

The free energy change for a process taking place with reactants and products present under nonstandard conditions, ΔG , is related to the standard free energy change, ΔG° , according to this equation:

Equation:

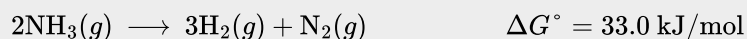
$$\Delta G = \Delta G^\circ + RT \ln Q$$

R is the gas constant (8.314 J/K mol), T is the kelvin or absolute temperature, and Q is the reaction quotient. We may use this equation to predict the spontaneity for a process under any given set of conditions as illustrated in [\[link\]](#).

Example:**Calculating ΔG under Nonstandard Conditions**

What is the free energy change for the process shown here under the specified conditions?

$T = 25^\circ\text{C}$, $P_{\text{N}_2} = 0.870 \text{ atm}$, $P_{\text{H}_2} = 0.250 \text{ atm}$, and $P_{\text{NH}_3} = 12.9 \text{ atm}$

Equation:**Solution**

The equation relating free energy change to standard free energy change and reaction quotient may be used directly:

Equation:

$$\Delta G = \Delta G^\circ + RT \ln Q = 33.0 \frac{\text{kJ}}{\text{mol}} + \left(8.314 \frac{\text{J}}{\text{mol K}} \times 298 \text{ K} \times \ln \frac{(0.250^3) \times 0.870}{12.9^2} \right) = 9680 \frac{\text{J}}{\text{mol}}$$

Since the computed value for ΔG is positive, the reaction is nonspontaneous under these conditions.

Check Your Learning

Calculate the free energy change for this same reaction at 875°C in a 5.00 L mixture containing 0.100 mol of each gas. Is the reaction spontaneous under these conditions?

Note:**Answer:**

$\Delta G = -47 \text{ kJ}$; yes

For a system at equilibrium, $Q = K$ and $\Delta G = 0$, and the previous equation may be written as

Equation:

$$0 = \Delta G^\circ + RT \ln K \qquad (\text{at equilibrium})$$

Equation:

$$\Delta G^\circ = -RT \ln K \qquad \text{or} \qquad K = e^{-\frac{\Delta G^\circ}{RT}}$$

This form of the equation provides a useful link between these two essential thermodynamic properties, and it can be used to derive equilibrium constants from standard free energy changes and vice versa. The relations between standard free energy changes and equilibrium constants are summarized in [\[link\]](#).

Relations between Standard Free Energy Changes and Equilibrium Constants

K	ΔG°	Comments
> 1	< 0	Products are more abundant at equilibrium.
< 1	> 0	Reactants are more abundant at equilibrium.
$= 1$	$= 0$	Reactants and products are equally abundant at equilibrium.

Example:

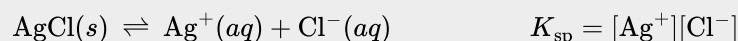
Calculating an Equilibrium Constant using Standard Free Energy Change

Given that the standard free energies of formation of $\text{Ag}^+(aq)$, $\text{Cl}^-(aq)$, and $\text{AgCl}(s)$ are 77.1 kJ/mol, -131.2 kJ/mol, and -109.8 kJ/mol, respectively, calculate the solubility product, K_{sp} , for AgCl.

Solution

The reaction of interest is the following:

Equation:



The standard free energy change for this reaction is first computed using standard free energies of formation for its reactants and products:

Equation:

$$\begin{aligned} \Delta G^\circ &= \Delta G_{298}^\circ = [\Delta G_f^\circ (\text{Ag}^+(aq)) + \Delta G_f^\circ (\text{Cl}^-(aq))] - [\Delta G_f^\circ (\text{AgCl}(s))] \\ &= [77.1 \text{ kJ/mol} - 131.2 \text{ kJ/mol}] - [-109.8 \text{ kJ/mol}] = 55.7 \text{ kJ/mol} \end{aligned}$$

The equilibrium constant for the reaction may then be derived from its standard free energy change:

Equation:

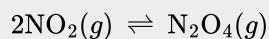
$$K_{\text{sp}} = e^{-\frac{\Delta G^\circ}{RT}} = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(-\frac{55.7 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol}\cdot\text{K} \times 298.15 \text{ K}}\right) = \exp(-22.470) = e^{-22.470} = 1.$$

This result is in reasonable agreement with the value provided in [Appendix J](#).

Check Your Learning

Use the thermodynamic data provided in [Appendix G](#) to calculate the equilibrium constant for the dissociation of dinitrogen tetroxide at 25 °C.

Equation:

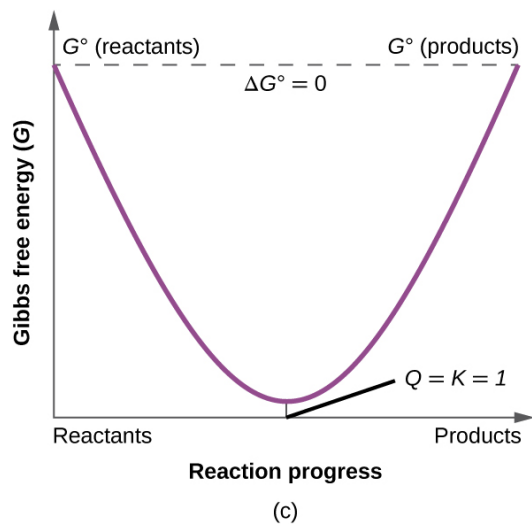
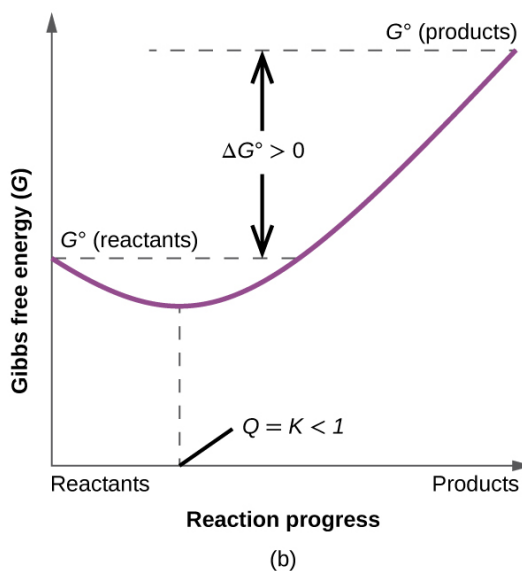
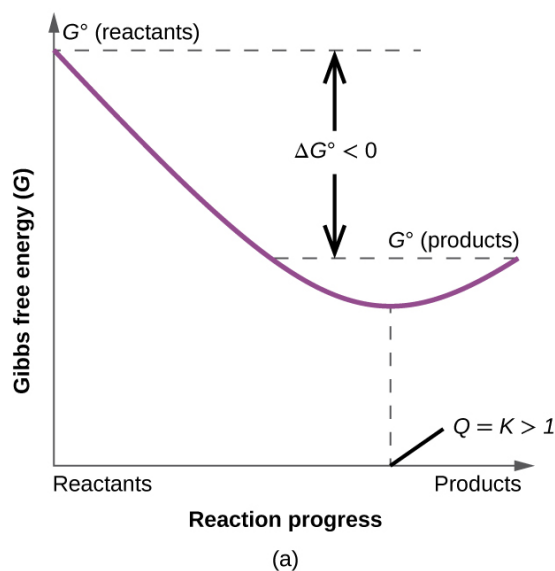


Note:

Answer:

$$K = 6.9$$

To further illustrate the relation between these two essential thermodynamic concepts, consider the observation that reactions spontaneously proceed in a direction that ultimately establishes equilibrium. As may be shown by plotting the free energy change versus the extent of the reaction (for example, as reflected in the value of Q), equilibrium is established when the system's free energy is minimized ([link](#)). If a system consists of reactants and products in nonequilibrium amounts ($Q \neq K$), the reaction will proceed spontaneously in the direction necessary to establish equilibrium.



These plots show the free energy versus reaction progress for systems whose standard free energy changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium.

Key Concepts and Summary

Gibbs free energy (G) is a state function defined with regard to system quantities only and may be used to predict the spontaneity of a process. A negative value for ΔG indicates a spontaneous process; a positive ΔG indicates a nonspontaneous process; and a ΔG of zero indicates that the system is at equilibrium. A number of approaches to the computation of free energy changes are possible.

Key Equations

- $\Delta G = \Delta H - T\Delta S$
- $\Delta G = \Delta G^\circ + RT \ln Q$
- $\Delta G^\circ = -RT \ln K$

Chemistry End of Chapter Exercises

Exercise:

Problem: What is the difference between ΔG , ΔG° , and ΔG_{298}° for a chemical change?

Exercise:

Problem:

A reaction has $\Delta H_{298}^\circ = 100 \text{ kJ/mol}$ and $\Delta S_{298}^\circ = 250 \text{ J/mol}\cdot\text{K}$. Is the reaction spontaneous at room temperature? If not, under what temperature conditions will it become spontaneous?

Solution:

The reaction is nonspontaneous at room temperature.

Above 400 K, ΔG will become negative, and the reaction will become spontaneous.

Exercise:

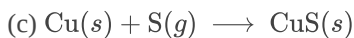
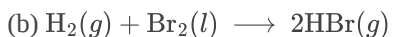
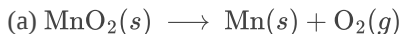
Problem:

Explain what happens as a reaction starts with $\Delta G < 0$ (negative) and reaches the point where $\Delta G = 0$.

Exercise:

Problem:

Use the standard free energy of formation data in [Appendix G](#) to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.



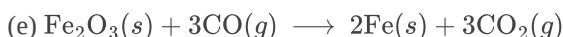
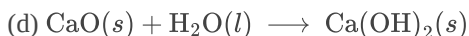
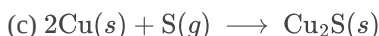
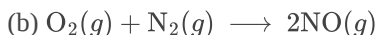
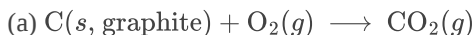
Solution:

(a) 465.1 kJ nonspontaneous; (b) -106.86 kJ spontaneous; (c) -53.6 kJ spontaneous; (d) -83.4 kJ spontaneous; (e) -406.7 kJ spontaneous; (f) -30.0 kJ spontaneous

Exercise:

Problem:

Use the standard free energy data in [Appendix G](#) to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.



Exercise:

Given:



(a) Determine the standard free energy of formation, ΔG_f° , for phosphoric acid.

(b) How does your calculated result compare to the value in [Appendix G](#)? Explain.

Solution:

(a) The standard free energy of formation is -1124.3 kJ/mol. (b) The calculation agrees with the value in [Appendix G](#) because free energy is a state function (just like the enthalpy and entropy), so its change depends only on the initial and final states, not the path between them.

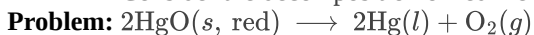
Exercise:

Problem:

Is the formation of ozone ($\text{O}_3(g)$) from oxygen ($\text{O}_2(g)$) spontaneous at room temperature under standard state conditions?

Exercise:

Consider the decomposition of red mercury(II) oxide under standard state conditions.



(a) Is the decomposition spontaneous under standard state conditions?

(b) Above what temperature does the reaction become spontaneous?

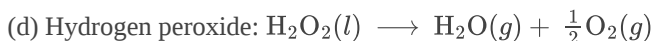
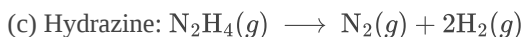
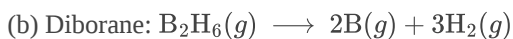
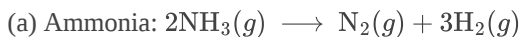
Solution:

(a) The reaction is nonspontaneous; (b) Above 566 °C the process is spontaneous.

Exercise:

Problem:

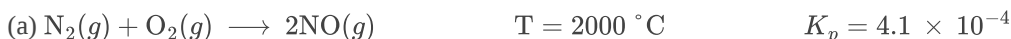
Among other things, an ideal fuel for the control thrusters of a space vehicle should decompose in a spontaneous exothermic reaction when exposed to the appropriate catalyst. Evaluate the following substances under standard state conditions as suitable candidates for fuels.



Exercise:

Problem:

Calculate ΔG° for each of the following reactions from the equilibrium constant at the temperature given.



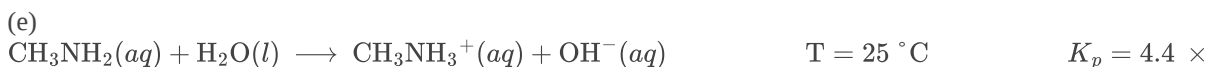
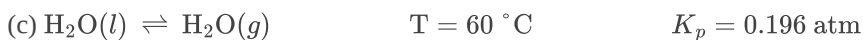
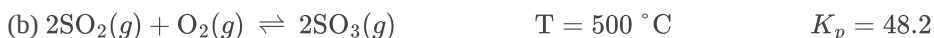
Solution:

(a) $1.5 \times 10^2\text{ kJ}$; (b) -21.9 kJ ; (c) -5.34 kJ ; (d) -0.383 kJ ; (e) 18 kJ ; (f) 71 kJ

Exercise:

Problem:

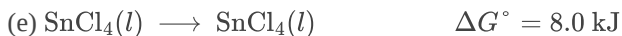
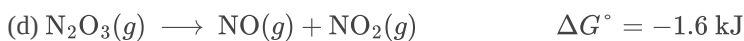
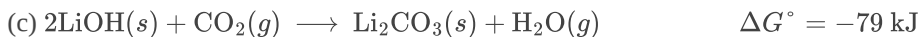
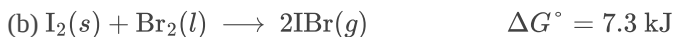
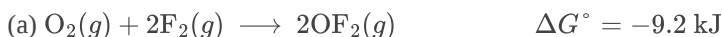
Calculate ΔG° for each of the following reactions from the equilibrium constant at the temperature given.



Exercise:

Problem:

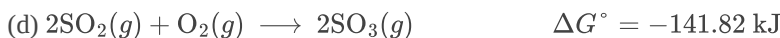
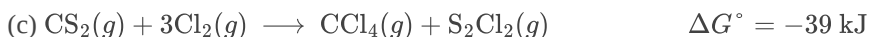
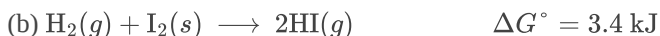
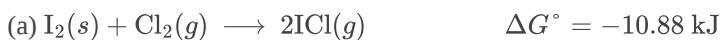
Calculate the equilibrium constant at 25 °C for each of the following reactions from the value of ΔG° given.

**Solution:**

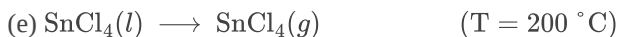
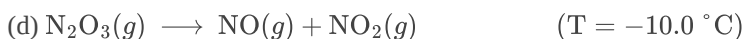
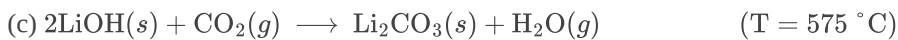
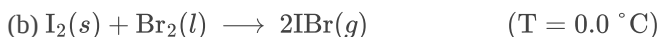
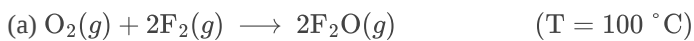
(a) $K = 41$; (b) $K = 0.053$; (c) $K = 6.9 \times 10^{13}$; (d) $K = 1.9$; (e) $K = 0.04$

Exercise:**Problem:**

Calculate the equilibrium constant at 25 °C for each of the following reactions from the value of ΔG° given.

**Exercise:**

Problem: Calculate the equilibrium constant at the temperature given.

**Solution:**

In each of the following, the value of ΔG is not given at the temperature of the reaction. Therefore, we must calculate ΔG from the values ΔH° and ΔS and then calculate ΔG from the relation $\Delta G = \Delta H^\circ - T\Delta S^\circ$.

(a) $K = 1.29$;

(b) $K = 2.51 \times 10^{-3}$;

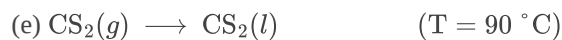
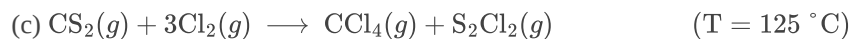
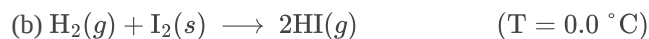
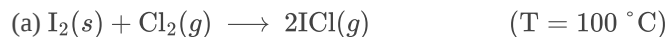
(c) $K = 4.83 \times 10^3$;

(d) $K = 0.219$;

(e) $K = 16.1$

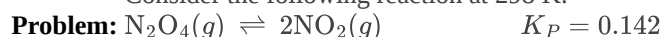
Exercise:

Problem: Calculate the equilibrium constant at the temperature given.



Exercise:

Consider the following reaction at 298 K:



What is the standard free energy change at this temperature? Describe what happens to the initial system, where the reactants and products are in standard states, as it approaches equilibrium.

Solution:

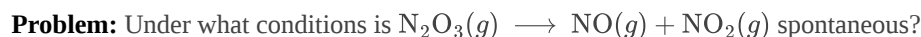
The standard free energy change is $\Delta G_{298}^\circ = -RT \ln K = 4.84 \text{ kJ/mol}$. When reactants and products are in their standard states (1 bar or 1 atm), $Q = 1$. As the reaction proceeds toward equilibrium, the reaction shifts left (the amount of products drops while the amount of reactants increases): $Q < 1$, and ΔG_{298} becomes less positive as it approaches zero. At equilibrium, $Q = K$, and $\Delta G = 0$.

Exercise:

Problem:

Determine the normal boiling point (in kelvin) of dichloroethane, CH_2Cl_2 . Find the actual boiling point using the Internet or some other source, and calculate the percent error in the temperature. Explain the differences, if any, between the two values.

Exercise:



Solution:

The reaction will be spontaneous at temperatures greater than 287 K.

Exercise:

Problem:

At room temperature, the equilibrium constant (K_w) for the self-ionization of water is 1.00×10^{-14} . Using this information, calculate the standard free energy change for the aqueous reaction of hydrogen ion with hydroxide ion to produce water. (Hint: The reaction is the reverse of the self-ionization reaction.)

Exercise:

Problem:

Hydrogen sulfide is a pollutant found in natural gas. Following its removal, it is converted to sulfur by the reaction $2\text{H}_2\text{S}(g) + \text{SO}_2(g) \rightleftharpoons \frac{3}{8}\text{S}_8(s, \text{ rhombic}) + 2\text{H}_2\text{O}(l)$. What is the equilibrium constant for this reaction? Is the reaction endothermic or exothermic?

Solution:

$$K = 5.35 \times 10^{15}$$

The process is exothermic.

Exercise:**Problem:**

Consider the decomposition of $\text{CaCO}_3(\text{s})$ into $\text{CaO}(\text{s})$ and $\text{CO}_2(\text{g})$. What is the equilibrium partial pressure of CO_2 at room temperature?

Exercise:**Problem:**

In the laboratory, hydrogen chloride ($\text{HCl}(\text{g})$) and ammonia ($\text{NH}_3(\text{g})$) often escape from bottles of their solutions and react to form the ammonium chloride ($\text{NH}_4\text{Cl}(\text{s})$), the white glaze often seen on glassware. Assuming that the number of moles of each gas that escapes into the room is the same, what is the maximum partial pressure of HCl and NH_3 in the laboratory at room temperature? (Hint: The partial pressures will be equal and are at their maximum value when at equilibrium.)

Solution:

1.0×10^{-8} atm. This is the maximum pressure of the gases under the stated conditions.

Exercise:**Problem:**

Benzene can be prepared from acetylene. $3\text{C}_2\text{H}_2(\text{g}) \rightleftharpoons \text{C}_6\text{H}_6(\text{g})$. Determine the equilibrium constant at 25 °C and at 850 °C. Is the reaction spontaneous at either of these temperatures? Why is all acetylene not found as benzene?

Exercise:**Problem:**

Carbon dioxide decomposes into CO and O_2 at elevated temperatures. What is the equilibrium partial pressure of oxygen in a sample at 1000 °C for which the initial pressure of CO_2 was 1.15 atm?

Solution:

$$x = 1.29 \times 10^{-5} \text{ atm} = P_{\text{O}_2}$$

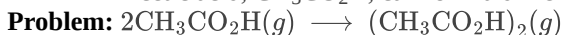
Exercise:**Problem:**

Carbon tetrachloride, an important industrial solvent, is prepared by the chlorination of methane at 850 K. $\text{CH}_4(\text{g}) + 4\text{Cl}_2(\text{g}) \longrightarrow \text{CCl}_4(\text{g}) + 4\text{HCl}(\text{g})$

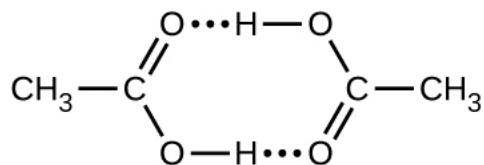
What is the equilibrium constant for the reaction at 850 K? Would the reaction vessel need to be heated or cooled to keep the temperature of the reaction constant?

Exercise:

Acetic acid, $\text{CH}_3\text{CO}_2\text{H}$, can form a dimer, $(\text{CH}_3\text{CO}_2\text{H})_2$, in the gas phase.



The dimer is held together by two hydrogen bonds with a total strength of 66.5 kJ per mole of dimer.



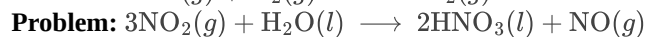
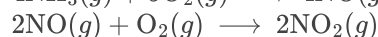
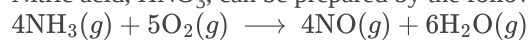
At 25 °C, the equilibrium constant for the dimerization is 1.3×10^3 (pressure in atm). What is ΔS° for the reaction?

Solution:

-0.16 kJ

Exercise:

Nitric acid, HNO_3 , can be prepared by the following sequence of reactions:



How much heat is evolved when 1 mol of $\text{NH}_3(g)$ is converted to $\text{HNO}_3(l)$? Assume standard states at 25 °C.

Exercise:

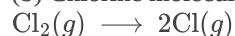
Problem: Determine ΔG° for the following reactions.

(a) Antimony pentachloride decomposes at 448 °C. The reaction is:



An equilibrium mixture in a 5.00 L flask at 448 °C contains 3.85 g of SbCl_5 , 9.14 g of SbCl_3 , and 2.84 g of Cl_2 .

(b) Chlorine molecules dissociate according to this reaction:



1.00% of Cl_2 molecules dissociate at 975 K and a pressure of 1.00 atm.

Solution:

(a) 22.1 kJ;

(b) 61.6 kJ/mol

Exercise:

Problem:

Given that the ΔG_f° for $\text{Pb}^{2+}(aq)$ and $\text{Cl}^-(aq)$ is -24.3 kJ/mole and -131.2 kJ/mole respectively, determine the solubility product, K_{sp} , for $\text{PbCl}_2(s)$.

Exercise:

Problem:

Determine the standard free energy change, ΔG_f° , for the formation of $\text{S}^{2-}(aq)$ given that the ΔG_f° for $\text{Ag}^+(aq)$ and $\text{Ag}_2\text{S}(s)$ are 77.1 kJ/mole and -39.5 kJ/mole respectively, and the solubility product for $\text{Ag}_2\text{S}(s)$ is 8×10^{-51} .

Solution:

90 kJ/mol

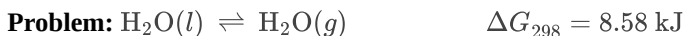
Exercise:

Problem:

Determine the standard enthalpy change, entropy change, and free energy change for the conversion of diamond to graphite. Discuss the spontaneity of the conversion with respect to the enthalpy and entropy changes. Explain why diamond spontaneously changing into graphite is not observed.

Exercise:

The evaporation of one mole of water at 298 K has a standard free energy change of 8.58 kJ.



- (a) Is the evaporation of water under standard thermodynamic conditions spontaneous?
- (b) Determine the equilibrium constant, K_p , for this physical process.
- (c) By calculating ΔG , determine if the evaporation of water at 298 K is spontaneous when the partial pressure of water, $P_{\text{H}_2\text{O}}$, is 0.011 atm.
- (d) If the evaporation of water were always nonspontaneous at room temperature, wet laundry would never dry when placed outside. In order for laundry to dry, what must be the value of $P_{\text{H}_2\text{O}}$ in the air?

Solution:

(a) Under standard thermodynamic conditions, the evaporation is nonspontaneous; (b) $K_p = 0.031$; (c) The evaporation of water is spontaneous; (d) $P_{\text{H}_2\text{O}}$ must always be less than K_p or less than 0.031 atm. 0.031 atm represents air saturated with water vapor at 25 °C, or 100% humidity.

Exercise:

Problem:

In glycolysis, the reaction of glucose (Glu) to form glucose-6-phosphate (G6P) requires ATP to be present as described by the following equation:



In this process, ATP becomes ADP summarized by the following equation:



Determine the standard free energy change for the following reaction, and explain why ATP is necessary to drive this process:



Exercise:

Problem:

One of the important reactions in the biochemical pathway glycolysis is the reaction of glucose-6-phosphate (G6P) to form fructose-6-phosphate (F6P):



- (a) Is the reaction spontaneous or nonspontaneous under standard thermodynamic conditions?
- (b) Standard thermodynamic conditions imply the concentrations of G6P and F6P to be 1 M, however, in a typical cell, they are not even close to these values. Calculate ΔG when the concentrations of G6P and F6P

are 120 μM and 28 μM respectively, and discuss the spontaneity of the forward reaction under these conditions. Assume the temperature is 37 $^{\circ}\text{C}$.

Solution:

(a) Nonspontaneous as $\Delta G_{298}^{\circ} > 0$; (b) $\Delta G = \Delta G^{\circ} + RT \ln Q$,
 $\Delta G = 1.7 \times 10^3 + (8.314 \times 310 \times \ln \frac{28}{120}) = -2.1 \text{ kJ}$. The forward reaction to produce F6P is spontaneous under these conditions.

Exercise:

Problem:

Without doing a numerical calculation, determine which of the following will reduce the free energy change for the reaction, that is, make it less positive or more negative, when the temperature is increased. Explain.

- (a) $\text{N}_2(g) + 3\text{H}_2(g) \longrightarrow 2\text{NH}_3(g)$
- (b) $\text{HCl}(g) + \text{NH}_3(g) \longrightarrow \text{NH}_4\text{Cl}(s)$
- (c) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7(s) \longrightarrow \text{Cr}_2\text{O}_3(s) + 4\text{H}_2\text{O}(g) + \text{N}_2(g)$
- (d) $2\text{Fe}(s) + 3\text{O}_2(g) \longrightarrow \text{Fe}_2\text{O}_3(s)$

Exercise:

Problem:

When ammonium chloride is added to water and stirred, it dissolves spontaneously and the resulting solution feels cold. Without doing any calculations, deduce the signs of ΔG , ΔH , and ΔS for this process, and justify your choices.

Solution:

ΔG is negative as the process is spontaneous. ΔH is positive as with the solution becoming cold, the dissolving must be endothermic. ΔS must be positive as this drives the process, and it is expected for the dissolution of any soluble ionic compound.

Exercise:

Problem:

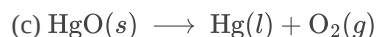
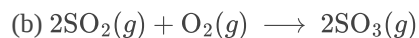
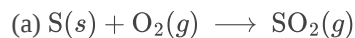
An important source of copper is from the copper ore, chalcocite, a form of copper(I) sulfide. When heated, the Cu_2S decomposes to form copper and sulfur described by the following equation:
 $\text{Cu}_2\text{S}(s) \longrightarrow \text{Cu}(s) + \text{S}(s)$

- (a) Determine ΔG_{298}° for the decomposition of $\text{Cu}_2\text{S}(s)$.
- (b) The reaction of sulfur with oxygen yields sulfur dioxide as the only product. Write an equation that describes this reaction, and determine ΔG_{298}° for the process.
- (c) The production of copper from chalcocite is performed by roasting the Cu_2S in air to produce the Cu. By combining the equations from Parts (a) and (b), write the equation that describes the roasting of the chalcocite, and explain why coupling these reactions together makes for a more efficient process for the production of the copper.

Exercise:

Problem:

What happens to ΔG (becomes more negative or more positive) for the following chemical reactions when the partial pressure of oxygen is increased?

**Solution:**

(a) Increasing the oxygen partial pressure will yield a decrease in Q and ΔG thus becomes more negative.

(b) Increasing the oxygen partial pressure will yield a decrease in Q and ΔG thus becomes more negative.

(c) Increasing the oxygen partial pressure will yield an increase in Q and ΔG thus becomes more positive.

Glossary

Gibbs free energy change (G)

thermodynamic property defined in terms of system enthalpy and entropy; all spontaneous processes involve a decrease in G

standard free energy change (ΔG°)

change in free energy for a process occurring under standard conditions (1 bar pressure for gases, 1 M concentration for solutions)

standard free energy of formation (ΔG_f°)

change in free energy accompanying the formation of one mole of substance from its elements in their standard states

Introduction

class="introduction"

- Balancing Oxidation-Reduction Reactions
- Galvanic Cells
- Standard Reduction Potentials
- The Nernst Equation
- Batteries and Fuel Cells
- Corrosion
- Electrolysis

Electric
vehicles
contain
batteries
that can be
recharged,
thereby
using
electric
energy to
bring about
a chemical
change and
vice versa.

(credit:
modificatio
n of work
by Robert
Couse-
Baker)



Electrochemistry deals with chemical reactions that produce electricity and the changes associated with the passage of electrical current through matter. The reactions involve electron transfer, and so they are oxidation-reduction (or redox) reactions. Many metals may be purified or electroplated using electrochemical methods. Devices such as automobiles, smartphones, electronic tablets, watches, pacemakers, and many others use batteries for power. Batteries use spontaneous chemical reactions to produce electricity that can be converted into useful work. All electrochemical systems involve the transfer of electrons. In many systems, the reactions occur in a region known as the cell, where the transfer of electrons occurs at electrodes.

Balancing Oxidation-Reduction Reactions

By the end of this section, you will be able to:

- Define electrochemistry and a number of important associated terms
- Split oxidation-reduction reactions into their oxidation half-reactions and reduction half-reactions
- Produce balanced oxidation-reduction equations for reactions in acidic or basic solution
- Identify oxidizing agents and reducing agents

Electricity refers to a number of phenomena associated with the presence and flow of electric charge. Electricity includes such diverse things as lightning, static electricity, the current generated by a battery as it discharges, and many other influences on our daily lives. The flow or movement of charge is an electric current ([link](#)). Electrons or ions may carry the charge. The elementary unit of charge is the charge of a proton, which is equal in magnitude to the charge of an electron. The SI unit of charge is the coulomb (C) and the charge of a proton is 1.602×10^{-19} C. The presence of an electric charge generates an electric field. Electric **current** is the rate of flow of charge. The SI unit for electrical current is the SI base unit called the ampere (A), which is a flow rate of 1 coulomb of charge per second ($1 \text{ A} = 1 \text{ C/s}$). An electric current flows in a path, called an electric **circuit**. In most chemical systems, it is necessary to maintain a closed path for current to flow. The flow of charge is generated by an electrical potential difference, or potential, between two points in the circuit. **Electrical potential** is the ability of the electric field to do work on the charge. The SI unit of electrical potential is the volt (V). When 1 coulomb of charge moves through a potential difference of 1 volt, it gains or loses 1 joule (J) of energy. [link](#) summarizes some of this information about electricity.

Common Electrical Terms		
Quantity	Definition	Measure or Unit
Electric charge	Charge on a proton	$1.602 \times 10^{-19} \text{ C}$
Electric current	The movement of charge	ampere = $\text{A} = 1 \text{ C/s}$
Electric potential	The force trying to move the charge	volt = $\text{V} = \text{J/C}$
Electric field	The force acting upon other charges in the vicinity	

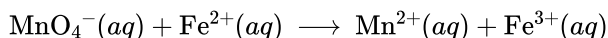


Electricity-related phenomena include lightning, accumulation of static electricity, and current produced by a battery. (credit left: modification of work by Thomas Bresson; credit middle: modification of work by Chris Darling; credit right: modification of work by Windell Oskay)

Electrochemistry studies oxidation-reduction reactions, which were first discussed in an earlier chapter, where we learned that oxidation was the loss of electrons and reduction was the gain of electrons. The reactions discussed tended to be rather simple, and conservation of mass (atom counting by type) and deriving a correctly balanced chemical equation were relatively simple. In this section, we will concentrate on the half-reaction method for balancing oxidation-reduction reactions. The use of half-reactions is important partly for balancing more complicated reactions and partly because many aspects of electrochemistry are easier to discuss in terms of half-reactions. There are alternate methods of balancing these reactions; however, there are no good alternatives to half-reactions for discussing what is occurring in many systems. The **half-reaction method** splits oxidation-reduction reactions into their oxidation “half” and reduction “half” to make finding the overall equation easier.

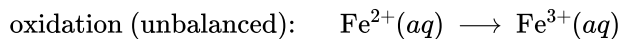
Electrochemical reactions frequently occur in solutions, which could be acidic, basic, or neutral. When balancing oxidation-reduction reactions, the nature of the solution may be important. It helps to see this in an actual problem. Consider the following unbalanced oxidation-reduction reaction in acidic solution:

Equation:



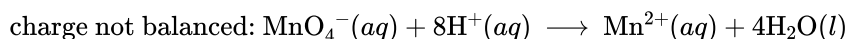
We can start by collecting the species we have so far into an unbalanced oxidation half-reaction and an unbalanced **reduction half-reaction**. Each of these half-reactions contain the same element in two different oxidation states. The Fe^{2+} has lost an electron to become Fe^{3+} ; therefore, the iron underwent oxidation. The reduction is not as obvious; however, the manganese gained five electrons to change from Mn^{7+} to Mn^{2+} .

Equation:



In acidic solution, there are hydrogen ions present, which are often useful in balancing half-reactions. It may be necessary to use the hydrogen ions directly or as a reactant that may react with oxygen to generate water. Hydrogen ions are very important in acidic solutions where the reactants or products contain hydrogen and/or oxygen. In this example, the oxidation half-reaction involves neither hydrogen nor oxygen, so hydrogen ions are not necessary to the balancing. However, the reduction half-reaction does involve oxygen. It is necessary to use hydrogen ions to convert this oxygen to water.

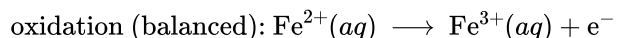
Equation:



The situation is different in basic solution because the hydrogen ion concentration is lower and the hydroxide ion concentration is higher. After finishing this example, we will examine how basic solutions differ from acidic solutions. A neutral solution may be treated as acidic or basic, though treating it as acidic is usually easier.

The iron atoms in the oxidation half-reaction are balanced (mass balance); however, the charge is unbalanced, since the charges on the ions are not equal. It is necessary to use electrons to balance the charge. The way to balance the charge is by *adding* electrons to one side of the equation. Adding a single electron on the right side gives a balanced oxidation half-reaction:

Equation:



You should check the half-reaction for the number of each atom type and the total charge on each side of the equation. The charges include the actual charges of the ions times the number of ions and the charge on an electron times the number of electrons.

Equation:

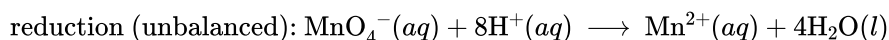
Fe: Does $(1 \times 1) = (1 \times 1)$? Yes.

Charge: Does $[1 \times (+2)] = [1 \times (+3) + 1 \times (-1)]$? Yes.

If the atoms and charges balance, the half-reaction is balanced. In oxidation half-reactions, electrons appear as products (on the right). As discussed in the earlier chapter, since iron underwent oxidation, iron is the reducing agent.

Now return to the reduction half-reaction equation:

Equation:



The atoms are balanced (mass balance), so it is now necessary to check for charge balance. The total charge on the left of the reaction arrow is $[(-1) \times (1) + (8) \times (+1)]$, or +7, while the total charge on the right side is $[(1) \times (+2) + (4) \times (0)]$, or +2. The difference between +7 and +2 is five; therefore, it is necessary to add five electrons to the left side to achieve charge balance.

Equation:



You should check this half-reaction for each atom type and for the charge, as well:

Equation:

Mn: Does $(1 \times 1) = (1 \times 1)$? Yes.

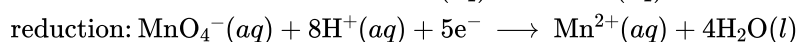
H: Does $(8 \times 1) = (4 \times 2)$? Yes.

O: Does $(1 \times 4) = (4 \times 1)$? Yes.

Charge: Does $[1 \times (-1) + 8 \times (+1) + 5 \times (-1)] = [1 \times (+2)]$? Yes.

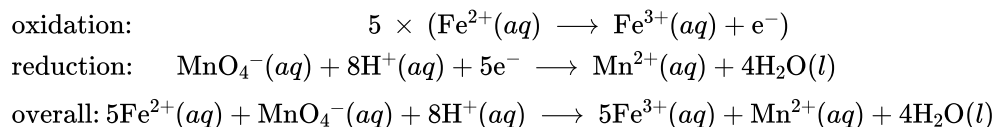
Now that this half-reaction is balanced, it is easy to see it involves reduction because electrons were gained when MnO_4^- was reduced to Mn^{2+} . In all reduction half-reactions, electrons appear as reactants (on the left side). As discussed in the earlier chapter, the species that was reduced, MnO_4^- in this case, is also called the oxidizing agent. We now have two balanced half-reactions.

Equation:



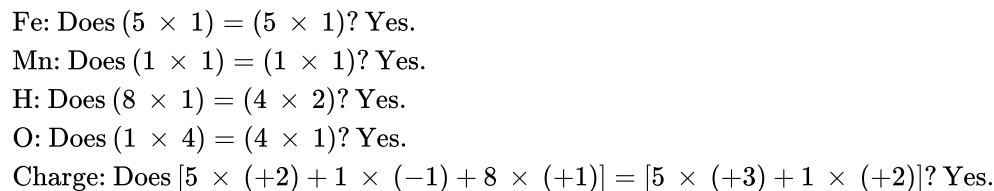
It is now necessary to combine the two halves to produce a whole reaction. The key to combining the half-reactions is the electrons. The electrons lost during oxidation must go somewhere. These electrons go on to cause reduction. The number of electrons transferred from the oxidation half-reaction to the reduction half-reaction must be equal. There can be no missing or excess electrons. In this example, the oxidation half-reaction generates one electron, while the reduction half-reaction requires five. The lowest common multiple of one and five is five; therefore, it is necessary to multiply every term in the oxidation half-reaction by five and every term in the reduction half-reaction by one. (In this case, the multiplication of the reduction half-reaction generates no change; however, this will not always be the case.) The multiplication of the two half-reactions by the appropriate factor followed by addition of the two halves gives

Equation:



The electrons do not appear in the final answer because the oxidation electrons are the same electrons as the reduction electrons and they “cancel.” Carefully check each side of the overall equation to verify everything was combined correctly:

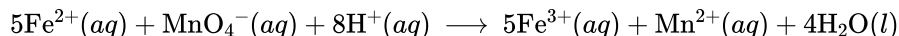
Equation:



Everything checks, so this is the overall equation in acidic solution. If something does not check, the most common error occurs during the multiplication of the individual half-reactions.

Now suppose we wanted the solution to be basic. Recall that basic solutions have excess hydroxide ions. Some of these hydroxide ions will react with hydrogen ions to produce water. The simplest way to generate the balanced overall equation in basic solution is to start with the balanced equation in acidic solution, then “convert” it to the equation for basic solution. However, it is necessary to exercise caution when doing this, as many reactants behave differently under basic conditions and many metal ions will precipitate as the metal hydroxide. We just produced the following reaction, which we want to change to a basic reaction:

Equation:



However, under basic conditions, MnO_4^{-} normally reduces to MnO_2 and iron will be present as either $\text{Fe}(\text{OH})_2$ or $\text{Fe}(\text{OH})_3$. For these reasons, under basic conditions, this reaction will be

Equation:

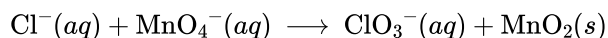


(Under very basic conditions MnO_4^{-} will reduce to MnO_4^{2-} , instead of MnO_2 .)

It is still possible to balance any oxidation-reduction reaction as an acidic reaction and then, when necessary, convert the equation to a basic reaction. There are very few examples in which the acidic and basic reactions will involve the same reactants and products. However, balancing a basic reaction as acidic and then converting to basic will work. To convert to a basic reaction, it is necessary to add the same number of hydroxide ions to each side of the equation so that all the hydrogen ions (H^{+}) are removed and mass balance is maintained. Hydrogen ion combines with hydroxide ion (OH^{-}) to produce water.

Let us now try a basic equation. We will start with the following basic reaction:

Equation:



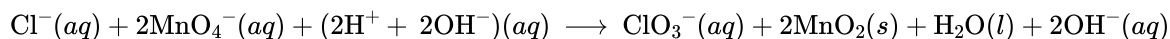
Balancing this as acid gives

Equation:



In this case, it is necessary to add two hydroxide ions to each side of the equation to convert the two hydrogen ions on the left into water:

Equation:

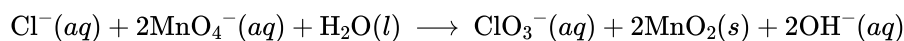


Equation:



Note that both sides of the equation show water. Simplifying should be done when possible. In this case, it is necessary to remove one H_2O from each side of the reaction arrow.

Equation:



Again, check each side of the overall equation to make sure there are no errors:

Equation:

Cl: Does $(1 \times 1) = (1 \times 1)$? Yes.

Mn: Does $(2 \times 1) = (2 \times 1)$? Yes.

H: Does $(1 \times 2) = (2 \times 1)$? Yes.

O: Does $(2 \times 4 + 1 \times 1) = (3 \times 1 + 2 \times 2 + 2 \times 1)$? Yes.

Charge: Does $[1 \times (-1) + 2 \times (-1)] = [1 \times (-1) + 2 \times (-1)]$? Yes.

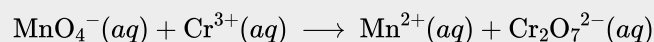
Everything checks, so this is the overall equation in basic solution.

Example:

Balancing Acidic Oxidation-Reduction Reactions

Balance the following reaction equation in acidic solution:

Equation:



Solution

This is an oxidation-reduction reaction, so start by collecting the species given into an unbalanced oxidation half-reaction and an unbalanced reduction half-reaction.

Equation:



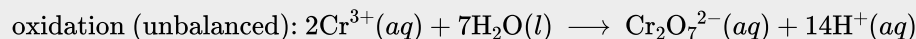
Starting with the oxidation half-reaction, we can balance the chromium

Equation:



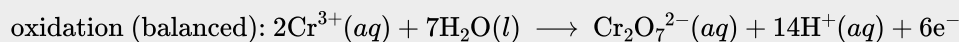
In acidic solution, we can use or generate hydrogen ions (H^+). Adding seven water molecules to the left side provides the necessary oxygen; the “left over” hydrogen appears as 14H^+ on the right:

Equation:



The left side of the equation has a total charge of $[2 \times (+3) = +6]$, and the right side a total charge of $[-2 + 14 \times (+1) = +12]$. The difference is six; adding six electrons to the right side produces a mass- and charge-balanced oxidation half-reaction (in acidic solution):

Equation:



Checking the half-reaction:

Equation:

Cr: Does $(2 \times 1) = (1 \times 2)$? Yes.

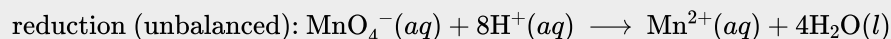
H: Does $(7 \times 2) = (14 \times 1)$? Yes.

O: Does $(7 \times 1) = (1 \times 7)$? Yes.

Charge: Does $[2 \times (+3)] = [1 \times (-2) + 14 \times (+1) + 6 \times (-1)]$? Yes.

Now work on the reduction. It is necessary to convert the four oxygen atoms in the permanganate into four water molecules. To do this, add eight H^+ to convert the oxygen into four water molecules:

Equation:



Then add five electrons to the left side to balance the charge:

Equation:



Make sure to check the half-reaction:

Equation:

Mn: Does $(1 \times 1) = (1 \times 1)$? Yes.

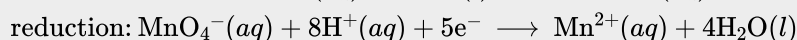
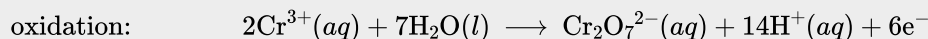
H: Does $(8 \times 1) = (4 \times 2)$? Yes.

O: Does $(1 \times 4) = (4 \times 1)$? Yes.

Charge: Does $[1 \times (-1) + 8 \times (+1) + 5 \times (-1)] = [1 \times (+2)]$? Yes.

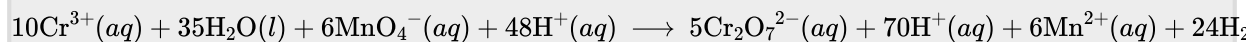
Collecting what we have so far:

Equation:

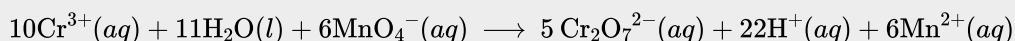


The least common multiple for the electrons is 30, so multiply the oxidation half-reaction by five, the reduction half-reaction by six, combine, and simplify:

Equation:



Equation:



Checking each side of the equation:

Equation:

Mn: Does $(6 \times 1) = (6 \times 1)$? Yes.

Cr: Does $(10 \times 1) = (5 \times 2)$? Yes.

H: Does $(11 \times 2) = (22 \times 1)$? Yes.

O: Does $(11 \times 1 + 6 \times 4) = (5 \times 7)$? Yes.

Charge: Does $[10 \times (+3) + 6 \times (-1)] = [5 \times (-2) + 22 \times (+1) + 6 \times (+2)]$? Yes.

This is the balanced equation in acidic solution.

Check your learning

Balance the following equation in acidic solution:

Equation:



Note:

Answer:

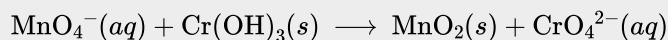


Example:

Balancing Basic Oxidation-Reduction Reactions

Balance the following reaction equation in basic solution:

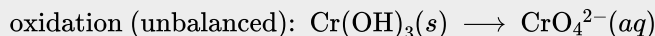
Equation:



Solution

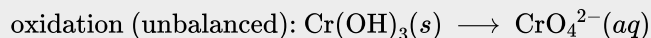
This is an oxidation-reduction reaction, so start by collecting the species given into an unbalanced oxidation half-reaction and an unbalanced reduction half-reaction

Equation:



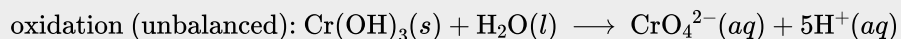
Starting with the oxidation half-reaction, we can balance the chromium

Equation:



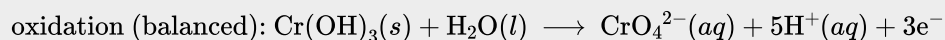
In acidic solution, we can use or generate hydrogen ions (H^+). Adding one water molecule to the left side provides the necessary oxygen; the “left over” hydrogen appears as five H^+ on the right side:

Equation:



The left side of the equation has a total charge of [0], and the right side a total charge of $[-2 + 5 \times (+1) = +3]$. The difference is three, adding three electrons to the right side produces a mass- and charge-balanced oxidation half-reaction (in acidic solution):

Equation:



Checking the half-reaction:

Equation:

Cr: Does $(1 \times 1) = (1 \times 1)$? Yes.

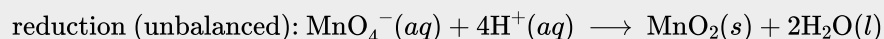
H: Does $(1 \times 3 + 1 \times 2) = (5 \times 1)$? Yes.

O: Does $(1 \times 3 + 1 \times 1) = (4 \times 1)$? Yes.

Charge: Does $[0 = [1 \times (-2) + 5 \times (+1) + 3 \times (-1)]]$? Yes.

Now work on the reduction. It is necessary to convert the four O atoms in the MnO_4^- minus the two O atoms in MnO_2 into two water molecules. To do this, add four H^+ to convert the oxygen into two water molecules:

Equation:



Then add three electrons to the left side to balance the charge:

Equation:



Make sure to check the half-reaction:

Equation:

Mn: Does $(1 \times 1) = (1 \times 1)$? Yes.

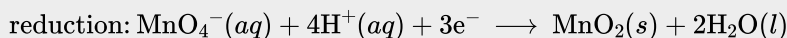
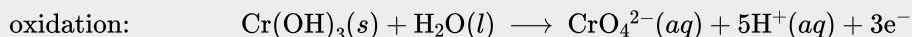
H: Does $(4 \times 1) = (2 \times 2)$? Yes.

O: Does $(1 \times 4) = (1 \times 2 + 2 \times 1)$? Yes.

Charge: Does $[1 \times (-1) + 4 \times (+1) + 3 \times (-1)] = [0]$? Yes.

Collecting what we have so far:

Equation:

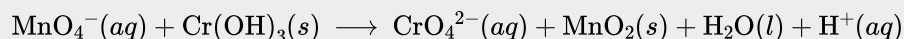


In this case, both half reactions involve the same number of electrons; therefore, simply add the two half-reactions together.

Equation:



Equation:



Checking each side of the equation:

Equation:

Mn: Does $(1 \times 1) = (1 \times 1)$? Yes.

Cr: Does $(1 \times 1) = (1 \times 1)$? Yes.

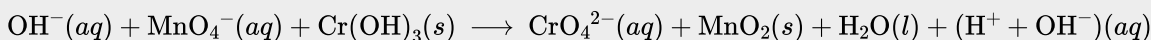
H: Does $(1 \times 3) = (2 \times 1 + 1 \times 1)$? Yes.

O: Does $(1 \times 4 + 1 \times 3) = (1 \times 4 + 1 \times 2 + 1 \times 1)$? Yes.

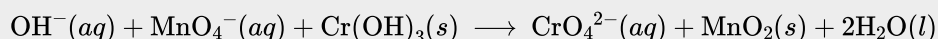
Charge: Does $[1 \times (-1)] = [1 \times (-2) + 1 \times (+1)]$? Yes.

This is the balanced equation in acidic solution. For a basic solution, add one hydroxide ion to each side and simplify:

Equation:



Equation:



Checking each side of the equation:

Equation:

Mn: Does $(1 \times 1) = (1 \times 1)$? Yes.

Cr: Does $(1 \times 1) = (1 \times 1)$? Yes.

H: Does $(1 \times 1 + 1 \times 3) = (2 \times 2)$? Yes.

O: Does $(1 \times 1 + 1 \times 4 + 1 \times 3) = (1 \times 4 + 1 \times 2 + 2 \times 1)$? Yes.

Charge: Does $[1 \times (-1) + 1 \times (-1)] = [1 \times (-2)]$? Yes.

This is the balanced equation in basic solution.

Check Your Learning

Balance the following in the type of solution indicated.

(a) $\text{H}_2 + \text{Cu}^{2+} \longrightarrow \text{Cu}$ (acidic solution)

(b) $\text{H}_2 + \text{Cu}(\text{OH})_2 \longrightarrow \text{Cu}$ (basic solution)

(c) $\text{Fe} + \text{Ag}^+ \longrightarrow \text{Fe}^{2+} + \text{Ag}$

(d) Identify the oxidizing agents in reactions (a), (b), and (c).

(e) Identify the reducing agents in reactions (a), (b), and (c).

Note:

Answer:

(a) $\text{H}_2(g) + \text{Cu}^{2+}(aq) \longrightarrow 2\text{H}^+(aq) + \text{Cu}(s)$; (b) $\text{H}_2(g) + \text{Cu}(\text{OH})_2(s) \longrightarrow 2\text{H}_2\text{O}(l) + \text{Cu}(s)$; (c) $\text{Fe}(s) + 2\text{Ag}^+(aq) \longrightarrow \text{Fe}^{2+}(aq) + 2\text{Ag}(s)$; (d) oxidizing agent = species reduced: Cu^{2+} , $\text{Cu}(\text{OH})_2$, Ag^+ (e) reducing agent = species oxidized: H_2 , H_2 , Fe .

Key Concepts and Summary

An electric current consists of moving charge. The charge may be in the form of electrons or ions. Current flows through an unbroken or closed circular path called a circuit. The current flows through a conducting medium as a result of a difference in electrical potential between two points in a circuit. Electrical potential has the units of energy per charge. In SI units, charge is measured in coulombs (C), current in amperes ($A = \frac{C}{s}$), and electrical potential in volts ($V = \frac{J}{C}$).

Oxidation is the loss of electrons, and the species that is oxidized is also called the reducing agent. Reduction is the gain of electrons, and the species that is reduced is also called the oxidizing agent. Oxidation-reduction reactions can be balanced using the half-reaction method. In this method, the oxidation-reduction reaction is split into an oxidation half-reaction and a reduction half-reaction. The oxidation half-reaction and reduction half-reaction are then balanced separately. Each of the half-reactions must have the same number of each type of atom on both sides of the equation *and* show the same total charge on each side of the equation. Charge is balanced in oxidation half-reactions by adding electrons as products; in reduction half-reactions, charge is balanced by adding electrons as reactants. The total number of electrons gained by reduction must exactly equal the number of electrons lost by oxidation when combining the two half-reactions to give the overall balanced equation. Balancing oxidation-reduction reaction equations in aqueous solutions frequently requires that oxygen or hydrogen be added or removed from a reactant. In acidic solution, hydrogen is added by adding hydrogen ion (H^+) and removed by producing hydrogen ion; oxygen is removed by adding hydrogen ion and producing water, and added by adding water and producing hydroxide ion. A balanced equation in basic solution can be obtained by first balancing the equation in acidic solution, and then adding hydroxide ion to each side of the balanced equation in such numbers that all the hydrogen ions are converted to water.

Chemistry End of Chapter Exercises

Exercise:

Problem:

If a 2.5 A current is run through a circuit for 35 minutes, how many coulombs of charge moved through the circuit?

Solution:

$$5.3 \times 10^3 \text{ C}$$

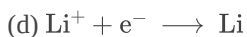
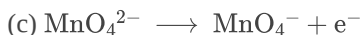
Exercise:

Problem: For the scenario in the previous question, how many electrons moved through the circuit?

Exercise:

Problem:

For each of the following balanced half-reactions, determine whether an oxidation or reduction is occurring.



Solution:

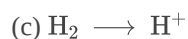
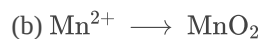
(a) reduction; (b) oxidation; (c) oxidation; (d) reduction

Exercise:

Problem:

For each of the following unbalanced half-reactions, determine whether an oxidation or reduction is occurring.

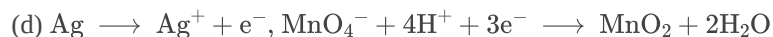
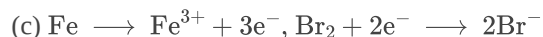
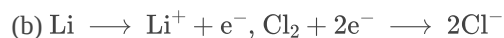
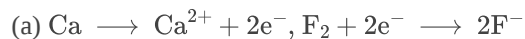




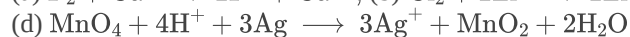
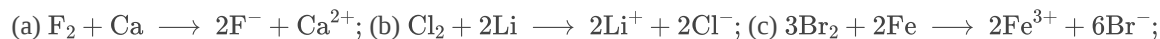
Exercise:

Problem:

Given the following pairs of balanced half-reactions, determine the balanced reaction for each pair of half-reactions in an acidic solution.

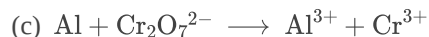
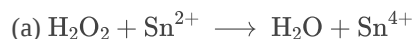


Solution:



Exercise:

Problem: Balance the following in acidic solution:



Exercise:

Problem:

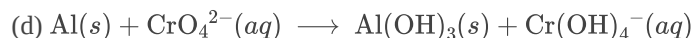
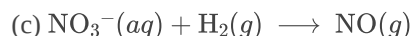
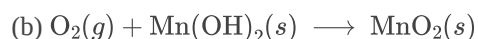
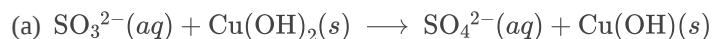
Identify the species that undergoes oxidation, the species that undergoes reduction, the oxidizing agent, and the reducing agent in each of the reactions of the previous problem.

Solution:

Oxidized: (a) Sn^{2+} ; (b) Hg ; (c) Al ; reduced: (a) H_2O_2 ; (b) PbO_2 ; (c) $\text{Cr}_2\text{O}_7^{2-}$; oxidizing agent: (a) H_2O_2 ; (b) PbO_2 ; (c) $\text{Cr}_2\text{O}_7^{2-}$; reducing agent: (a) Sn^{2+} ; (b) Hg ; (c) Al

Exercise:

Problem: Balance the following in basic solution:



Exercise:**Problem:**

Identify the species that was oxidized, the species that was reduced, the oxidizing agent, and the reducing agent in each of the reactions of the previous problem.

Solution:

Oxidized = reducing agent: (a) SO_3^{2-} ; (b) $\text{Mn}(\text{OH})_2$; (c) H_2 ; (d) Al ; reduced = oxidizing agent: (a) $\text{Cu}(\text{OH})_2$; (b) O_2 ; (c) NO_3^- ; (d) CrO_4^{2-}

Exercise:**Problem:**

Why is it not possible for hydroxide ion (OH^-) to appear in either of the half-reactions or the overall equation when balancing oxidation-reduction reactions in acidic solution?

Exercise:**Problem:**

Why is it not possible for hydrogen ion (H^+) to appear in either of the half-reactions or the overall equation when balancing oxidation-reduction reactions in basic solution?

Solution:

In basic solution, $[\text{OH}^-] > 1 \times 10^{-7} \text{ M} > [\text{H}^+]$. Hydrogen ion cannot appear as a reactant because its concentration is essentially zero. If it were produced, it would instantly react with the excess hydroxide ion to produce water. Thus, hydrogen ion should *not* appear as a reactant or product in basic solution.

Exercise:

Problem: Why must the charge balance in oxidation-reduction reactions?

Glossary

circuit

path taken by a current as it flows because of an electrical potential difference

current

flow of electrical charge; the SI unit of charge is the coulomb (C) and current is measured in amperes ($1 \text{ A} = 1 \frac{\text{C}}{\text{s}}$)

electrical potential

energy per charge; in electrochemical systems, it depends on the way the charges are distributed within the system; the SI unit of electrical potential is the volt ($1 \text{ V} = 1 \frac{\text{J}}{\text{C}}$)

half-reaction method

method that produces a balanced overall oxidation-reduction reaction by splitting the reaction into an oxidation “half” and reduction “half,” balancing the two half-reactions, and then combining the oxidation half-reaction and reduction half-reaction in such a way that the number of electrons generated by the oxidation is exactly canceled by the number of electrons required by the reduction

oxidation half-reaction

the “half” of an oxidation-reduction reaction involving oxidation; the half-reaction in which electrons appear as products; balanced when each atom type, as well as the charge, is balanced

reduction half-reaction

the “half” of an oxidation-reduction reaction involving reduction; the half-reaction in which electrons appear as reactants; balanced when each atom type, as well as the charge, is balanced

Galvanic Cells

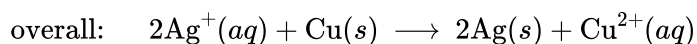
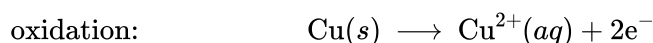
By the end of this section, you will be able to:

- Use cell notation to describe galvanic cells
- Describe the basic components of galvanic cells

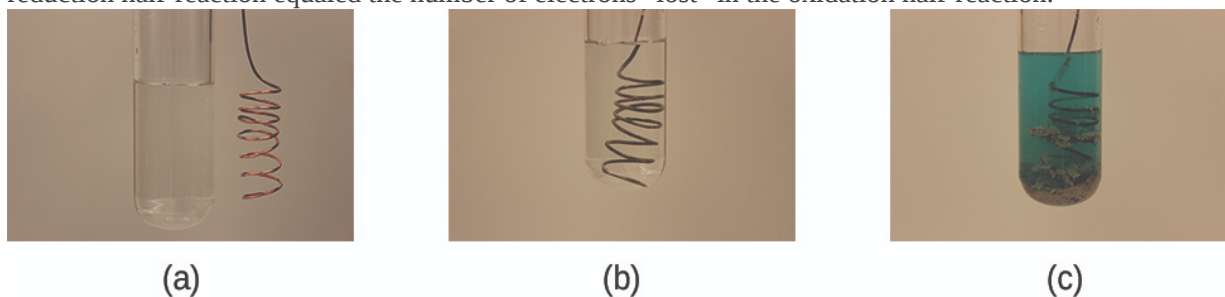
Galvanic cells, also known as **voltaic cells**, are electrochemical cells in which spontaneous oxidation-reduction reactions produce electrical energy. In writing the equations, it is often convenient to separate the oxidation-reduction reactions into half-reactions to facilitate balancing the overall equation and to emphasize the actual chemical transformations.

Consider what happens when a clean piece of copper metal is placed in a solution of silver nitrate ([link](#)). As soon as the copper metal is added, silver metal begins to form and copper ions pass into the solution. The blue color of the solution on the far right indicates the presence of copper ions. The reaction may be split into its two half-reactions. Half-reactions separate the oxidation from the reduction, so each can be considered individually.

Equation:



The equation for the reduction half-reaction had to be doubled so the number of electrons “gained” in the reduction half-reaction equaled the number of electrons “lost” in the oxidation half-reaction.



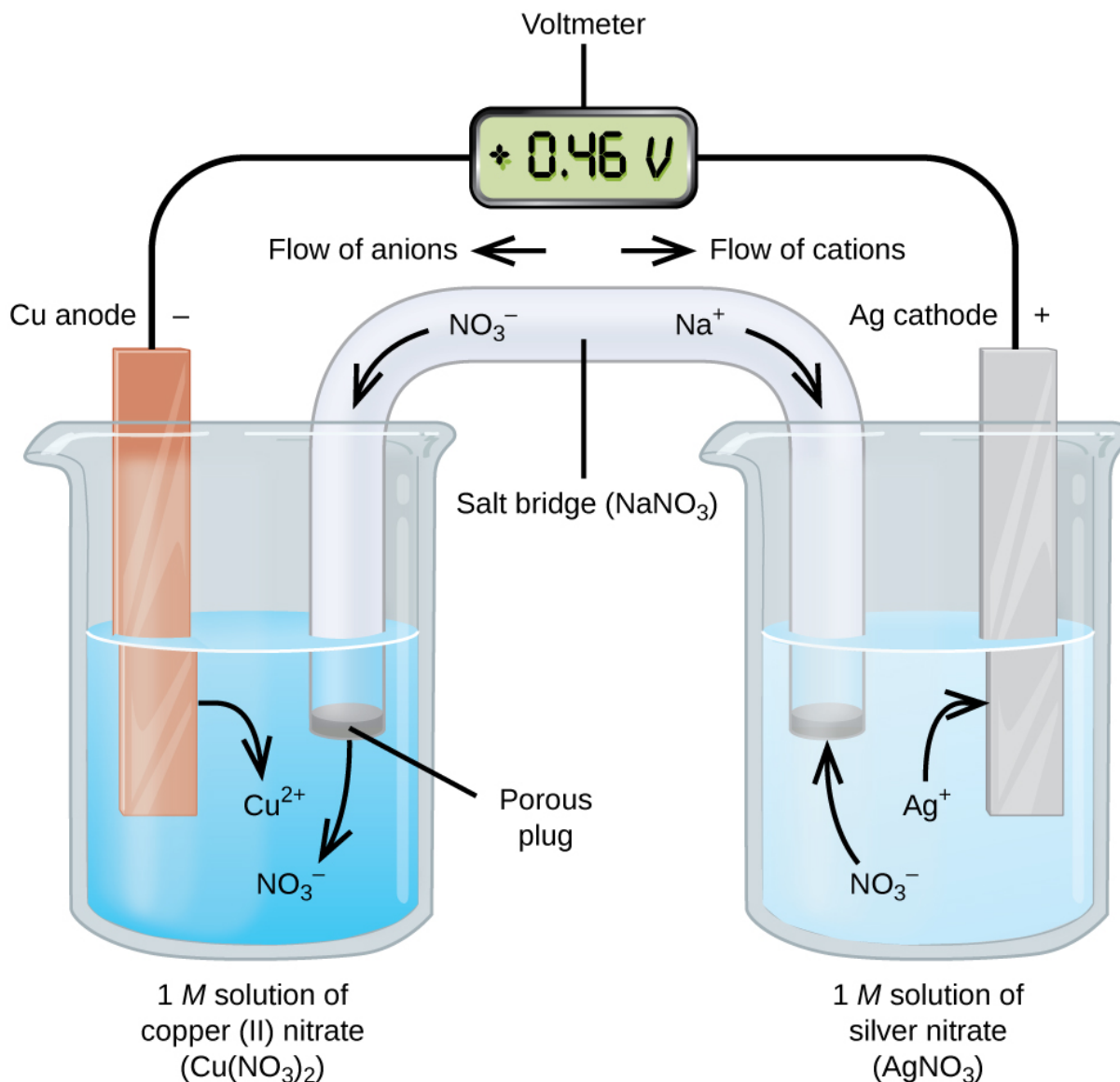
When a clean piece of copper metal is placed into a clear solution of silver nitrate (a), an oxidation-reduction reaction occurs that results in the exchange of Cu^{2+} for Ag^{+} ions in solution. As the reaction proceeds (b), the solution turns blue (c) because of the copper ions present, and silver metal is deposited on the copper strip as the silver ions are removed from solution. (credit: modification of work by Mark Ott)

Galvanic or voltaic cells involve spontaneous electrochemical reactions in which the half-reactions are separated ([link](#)) so that current can flow through an external wire. The beaker on the left side of the figure is called a half-cell, and contains a 1 M solution of copper(II) nitrate $[\text{Cu}(\text{NO}_3)_2]$ with a piece of copper metal partially submerged in the solution. The copper metal is an electrode. The copper is undergoing oxidation; the copper electrode is referred to as the **anode**. The anode is connected to a voltmeter with a wire and the other terminal of the voltmeter is connected to a silver electrode by a wire. The silver is undergoing reduction; the silver electrode is referred to as the **cathode**. The half-cell on the right side of the figure consists of the silver electrode in a 1 M solution of silver nitrate (AgNO_3). At this point, no current

flows—that is, no significant movement of electrons through the wire occurs because the circuit is open. The circuit is closed using a salt bridge, which transmits the current with moving ions. The salt bridge consists of a concentrated, nonreactive, electrolyte solution such as the sodium nitrate (NaNO_3) solution used in this example. As electrons flow from left to right through the electrode and wire, nitrate ions (anions) pass through the porous plug on the left into the copper(II) nitrate solution. This keeps the beaker on the left electrically neutral by neutralizing the charge on the copper(II) ions that are produced in the solution as the copper metal is oxidized. At the same time, the nitrate ions are moving to the left, sodium ions (cations) move to the right, through the porous plug, and into the silver nitrate solution on the right. These added cations “replace” the silver ions that are removed from the solution as they were reduced to silver metal, keeping the beaker on the right electrically neutral. Without the salt bridge, the compartments would not remain electrically neutral and no significant current would flow. However, if the two compartments are in direct contact, a salt bridge is not necessary. The instant the circuit is completed, the voltmeter reads +0.46 V, this is called the **cell potential**. The cell potential is created when the two dissimilar metals are connected, and is a measure of the energy per unit charge available from the oxidation-reduction reaction. The volt is the derived SI unit for electrical potential

Equation:

$$\text{volt} = V = \frac{\text{J}}{\text{C}}$$



In this standard galvanic cell, the half-cells are separated; electrons can flow through an external wire and become available to do electrical work.

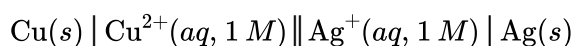
When the electrochemical cell is constructed in this fashion, a positive cell potential indicates a spontaneous reaction *and* that the electrons are flowing from the left to the right. There is a lot going on in [\[link\]](#), so it is useful to summarize things for this system:

- Electrons flow from the anode to the cathode: left to right in the standard galvanic cell in the figure.
- The electrode in the left half-cell is the anode because oxidation occurs here. The name refers to the flow of anions in the salt bridge toward it.
- The electrode in the right half-cell is the cathode because reduction occurs here. The name refers to the flow of cations in the salt bridge toward it.

- Oxidation occurs at the anode (the left half-cell in the figure).
- Reduction occurs at the cathode (the right half-cell in the figure).
- The cell potential, +0.46 V, in this case, results from the inherent differences in the nature of the materials used to make the two half-cells.
- The salt bridge must be present to close (complete) the circuit and both an oxidation and reduction must occur for current to flow.

There are many possible galvanic cells, so a shorthand notation is usually used to describe them. The **cell notation** (sometimes called a cell diagram) provides information about the various species involved in the reaction. This notation also works for other types of cells. A vertical line, $|$, denotes a phase boundary and a double line, \parallel , the salt bridge. Information about the anode is written to the left, followed by the anode solution, then the salt bridge (when present), then the cathode solution, and, finally, information about the cathode to the right. The cell notation for the galvanic cell in [\[link\]](#) is then

Equation:

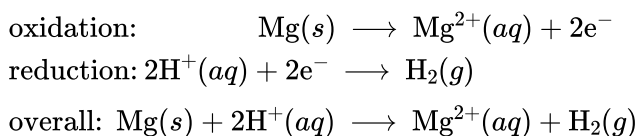


Note that spectator ions are not included and that the simplest form of each half-reaction was used. When known, the initial concentrations of the various ions are usually included.

One of the simplest cells is the Daniell cell. It is possible to construct this battery by placing a copper electrode at the bottom of a jar and covering the metal with a copper sulfate solution. A zinc sulfate solution is floated on top of the copper sulfate solution; then a zinc electrode is placed in the zinc sulfate solution. Connecting the copper electrode to the zinc electrode allows an electric current to flow. This is an example of a cell without a salt bridge, and ions may flow across the interface between the two solutions.

Some oxidation-reduction reactions involve species that are poor conductors of electricity, and so an electrode is used that does not participate in the reactions. Frequently, the electrode is platinum, gold, or graphite, all of which are inert to many chemical reactions. One such system is shown in [\[link\]](#). Magnesium undergoes oxidation at the anode on the left in the figure and hydrogen ions undergo reduction at the cathode on the right. The reaction may be summarized as

Equation:



The cell used an inert platinum wire for the cathode, so the cell notation is

Equation:



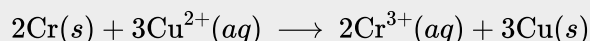
The magnesium electrode is an **active electrode** because it participates in the oxidation-reduction reaction. **Inert electrodes**, like the platinum electrode in [\[link\]](#), do not participate in the oxidation-reduction reaction and are present so that current can flow through the cell. Platinum or gold generally make good inert electrodes because they are chemically unreactive.

Example:

Using Cell Notation

Consider a galvanic cell consisting of

Equation:

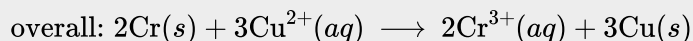
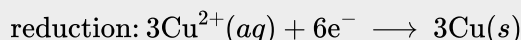
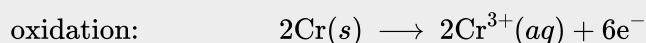


Write the oxidation and reduction half-reactions and write the reaction using cell notation. Which reaction occurs at the anode? The cathode?

Solution

By inspection, Cr is oxidized when three electrons are lost to form Cr^{3+} , and Cu^{2+} is reduced as it gains two electrons to form Cu. Balancing the charge gives

Equation:

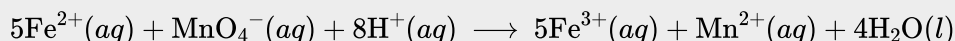


Cell notation uses the simplest form of each of the equations, and starts with the reaction at the anode. No concentrations were specified so: $\text{Cr}(s) \mid \text{Cr}^{3+}(aq) \parallel \text{Cu}^{2+}(aq) \mid \text{Cu}(s)$. Oxidation occurs at the anode and reduction at the cathode.

Using Cell Notation

Consider a galvanic cell consisting of

Equation:

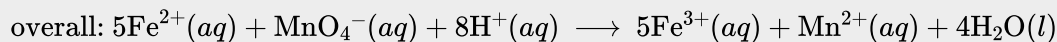
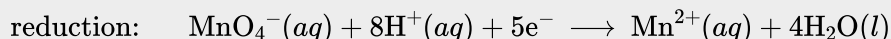


Write the oxidation and reduction half-reactions and write the reaction using cell notation. Which reaction occurs at the anode? The cathode?

Solution

By inspection, Fe^{2+} undergoes oxidation when one electron is lost to form Fe^{3+} , and MnO_4^{-} is reduced as it gains five electrons to form Mn^{2+} . Balancing the charge gives

Equation:



Cell notation uses the simplest form of each of the equations, and starts with the reaction at the anode. It is necessary to use an inert electrode, such as platinum, because there is no metal present to conduct the electrons from the anode to the cathode. No concentrations were specified so:

$\text{Pt}(s) \mid \text{Fe}^{2+}(aq), \text{Fe}^{3+}(aq) \parallel \text{MnO}_4^{-}(aq), \text{H}^{+}(aq), \text{Mn}^{2+}(aq) \mid \text{Pt}(s)$. Oxidation occurs at the anode and reduction at the cathode.

Check Your Learning

Use cell notation to describe the galvanic cell where copper(II) ions are reduced to copper metal and zinc metal is oxidized to zinc ions.

Note:

Answer:

From the information given in the problem:

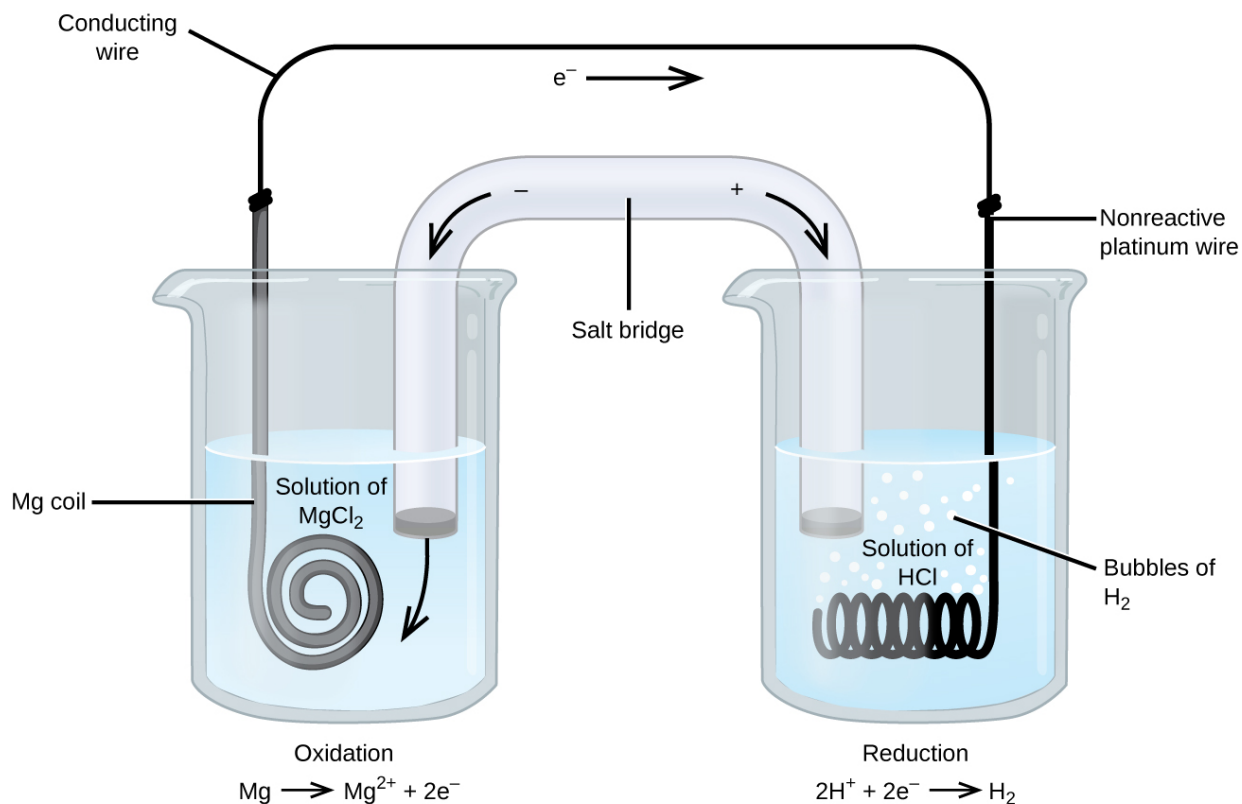
anode (oxidation): $\text{Zn}(s) \longrightarrow \text{Zn}^{2+}(aq) + 2e^{-}$

cathode (reduction): $\text{Cu}^{2+}(aq) + 2e^{-} \longrightarrow \text{Cu}(s)$

overall: $\text{Zn}(s) + \text{Cu}^{2+}(aq) \longrightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s)$

Using cell notation:

$\text{Zn}(s) \mid \text{Zn}^{2+}(aq) \parallel \text{Cu}^{2+}(aq) \mid \text{Cu}(s)$.



The oxidation of magnesium to magnesium ion occurs in the beaker on the left side in this apparatus; the reduction of hydrogen ions to hydrogen occurs in the beaker on the right. A nonreactive, or inert, platinum wire allows electrons from the left beaker to move into the right beaker. The overall reaction

is: $\text{Mg} + 2\text{H}^{+} \longrightarrow \text{Mg}^{2+} + \text{H}_2$, which is represented in cell notation as:

$\text{Mg}(s) \mid \text{Mg}^{2+}(aq) \parallel \text{H}^{+}(aq) \mid \text{H}_2(g) \mid \text{Pt}(s)$.

Key Concepts and Summary

Electrochemical cells typically consist of two half-cells. The half-cells separate the oxidation half-reaction from the reduction half-reaction and make it possible for current to flow through an external wire. One half-cell, normally depicted on the left side in a figure, contains the anode. Oxidation occurs at the anode. The

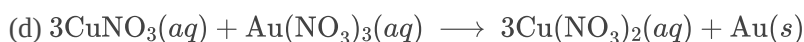
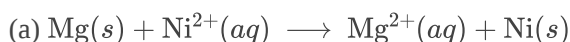
anode is connected to the cathode in the other half-cell, often shown on the right side in a figure. Reduction occurs at the cathode. Adding a salt bridge completes the circuit allowing current to flow. Anions in the salt bridge flow toward the anode and cations in the salt bridge flow toward the cathode. The movement of these ions completes the circuit and keeps each half-cell electrically neutral. Electrochemical cells can be described using cell notation. In this notation, information about the reaction at the anode appears on the left and information about the reaction at the cathode on the right. The salt bridge is represented by a double line, \parallel . The solid, liquid, or aqueous phases within a half-cell are separated by a single line, $|$. The phase and concentration of the various species is included after the species name. Electrodes that participate in the oxidation-reduction reaction are called active electrodes. Electrodes that do not participate in the oxidation-reduction reaction but are there to allow current to flow are inert electrodes. Inert electrodes are often made from platinum or gold, which are unchanged by many chemical reactions.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Write the following balanced reactions using cell notation. Use platinum as an inert electrode, if needed.



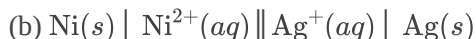
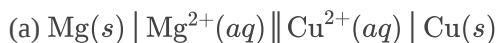
Solution:

(a) $\text{Mg}(s) \mid \text{Mg}^{2+}(aq) \parallel \text{Ni}^{2+}(aq) \mid \text{Ni}(s)$; (b) $\text{Cu}(s) \mid \text{Cu}^{2+}(aq) \parallel \text{Ag}^+(aq) \mid \text{Ag}(s)$; (c) $\text{Mn}(s) \mid \text{Mn}^{2+}(aq) \parallel \text{Sn}^{2+}(aq) \mid \text{Sn}(s)$; (d) $\text{Pt}(s) \mid \text{Cu}^+(aq), \text{Cu}^{2+}(aq) \parallel \text{Au}^{3+}(aq) \mid \text{Au}(s)$

Exercise:

Problem:

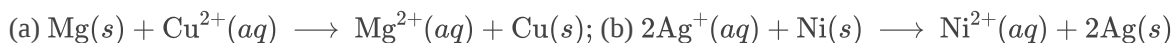
Given the following cell notations, determine the species oxidized, species reduced, and the oxidizing agent and reducing agent, without writing the balanced reactions.



Exercise:

Problem: For the cell notations in the previous problem, write the corresponding balanced reactions.

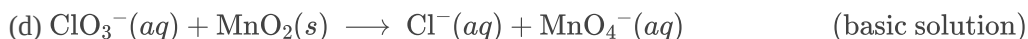
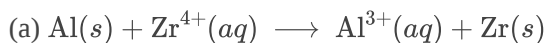
Solution:



Exercise:

Problem:

Balance the following reactions and write the reactions using cell notation. Ignore any inert electrodes, as they are never part of the half-reactions.

**Exercise:****Problem:**

Identify the species oxidized, species reduced, and the oxidizing agent and reducing agent for all the reactions in the previous problem.

Solution:

Species oxidized = reducing agent: (a) $\text{Al}(s)$; (b) $\text{NO}(g)$; (c) $\text{Mg}(s)$; and (d) $\text{MnO}_2(s)$; Species reduced = oxidizing agent: (a) $\text{Zr}^{4+}(aq)$; (b) $\text{Ag}^+(aq)$; (c) $\text{SiO}_3^{2-}(aq)$; and (d) $\text{ClO}_3^-(aq)$

Exercise:

Problem: From the information provided, use cell notation to describe the following systems:

(a) In one half-cell, a solution of $\text{Pt}(\text{NO}_3)_2$ forms Pt metal, while in the other half-cell, Cu metal goes into a $\text{Cu}(\text{NO}_3)_2$ solution with all solute concentrations 1 M.

(b) The cathode consists of a gold electrode in a 0.55 M $\text{Au}(\text{NO}_3)_3$ solution and the anode is a magnesium electrode in 0.75 M $\text{Mg}(\text{NO}_3)_2$ solution.

(c) One half-cell consists of a silver electrode in a 1 M AgNO_3 solution, and in the other half-cell, a copper electrode in 1 M $\text{Cu}(\text{NO}_3)_2$ is oxidized.

Exercise:

Problem: Why is a salt bridge necessary in galvanic cells like the one in [\[link\]](#)?

Solution:

Without the salt bridge, the circuit would be open (or broken) and no current could flow. With a salt bridge, each half-cell remains electrically neutral and current can flow through the circuit.

Exercise:**Problem:**

An active (metal) electrode was found to gain mass as the oxidation-reduction reaction was allowed to proceed. Was the electrode part of the anode or cathode? Explain.

Exercise:

Problem:

An active (metal) electrode was found to lose mass as the oxidation-reduction reaction was allowed to proceed. Was the electrode part of the anode or cathode? Explain.

Solution:

Active electrodes participate in the oxidation-reduction reaction. Since metals form cations, the electrode would lose mass if metal atoms in the electrode were to oxidize and go into solution. Oxidation occurs at the anode.

Exercise:**Problem:**

The mass of three different metal electrodes, each from a different galvanic cell, were determined before and after the current generated by the oxidation-reduction reaction in each cell was allowed to flow for a few minutes. The first metal electrode, given the label A, was found to have increased in mass; the second metal electrode, given the label B, did not change in mass; and the third metal electrode, given the label C, was found to have lost mass. Make an educated guess as to which electrodes were active and which were inert electrodes, and which were anode(s) and which were the cathode(s).

Glossary**active electrode**

electrode that participates in the oxidation-reduction reaction of an electrochemical cell; the mass of an active electrode changes during the oxidation-reduction reaction

anode

electrode in an electrochemical cell at which oxidation occurs; information about the anode is recorded on the left side of the salt bridge in cell notation

cathode

electrode in an electrochemical cell at which reduction occurs; information about the cathode is recorded on the right side of the salt bridge in cell notation

cell notation

shorthand way to represent the reactions in an electrochemical cell

cell potential

difference in electrical potential that arises when dissimilar metals are connected; the driving force for the flow of charge (current) in oxidation-reduction reactions

galvanic cell

electrochemical cell that involves a spontaneous oxidation-reduction reaction; electrochemical cells with positive cell potentials; also called a voltaic cell

inert electrode

electrode that allows current to flow, but that does not otherwise participate in the oxidation-reduction reaction in an electrochemical cell; the mass of an inert electrode does not change during the oxidation-reduction reaction; inert electrodes are often made of platinum or gold because these metals are chemically unreactive.

voltaic cell

another name for a galvanic cell

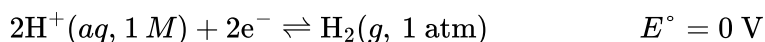
Standard Reduction Potentials

By the end of this section, you will be able to:

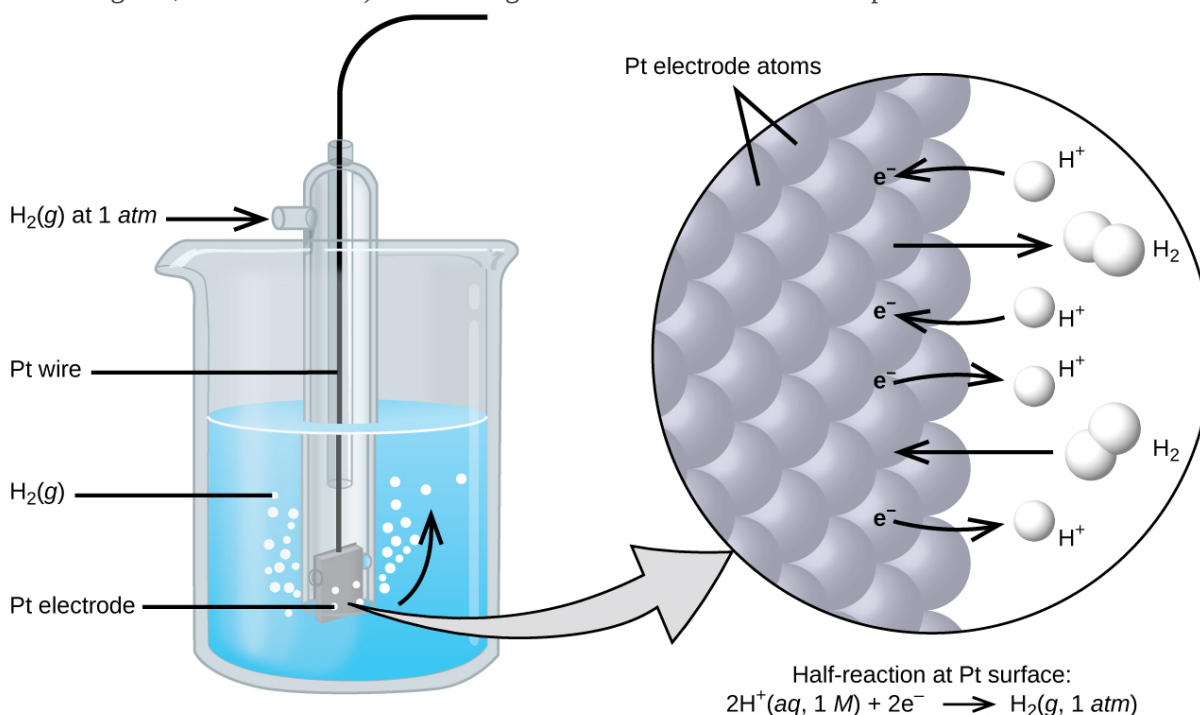
- Determine standard cell potentials for oxidation-reduction reactions
- Use standard reduction potentials to determine the better oxidizing or reducing agent from among several possible choices

The cell potential in [link](#) (+0.46 V) results from the difference in the electrical potentials for each electrode. While it is impossible to determine the electrical potential of a single electrode, we can assign an electrode the value of zero and then use it as a reference. The electrode chosen as the zero is shown in [link](#) and is called the **standard hydrogen electrode (SHE)**. The SHE consists of 1 atm of hydrogen gas bubbled through a 1 M HCl solution, usually at room temperature. Platinum, which is chemically inert, is used as the electrode. The reduction half-reaction chosen as the reference is

Equation:



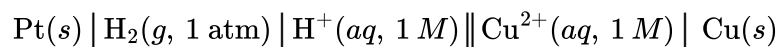
E° is the standard reduction potential. The superscript “°” on the E denotes standard conditions (1 bar or 1 atm for gases, 1 M for solutes). This voltage is defined as zero for all temperatures.



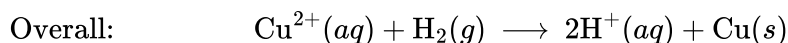
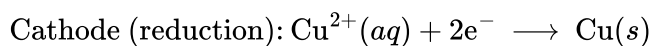
Hydrogen gas at 1 atm is bubbled through 1 M HCl solution. Platinum, which is inert to the action of the 1 M HCl, is used as the electrode. Electrons on the surface of the electrode combine with H^+ in solution to produce hydrogen gas.

A galvanic cell consisting of a SHE and Cu^{2+}/Cu half-cell can be used to determine the standard reduction potential for Cu^{2+} ([link](#)). In cell notation, the reaction is

Equation:



Electrons flow from the anode to the cathode. The reactions, which are reversible, are
Equation:



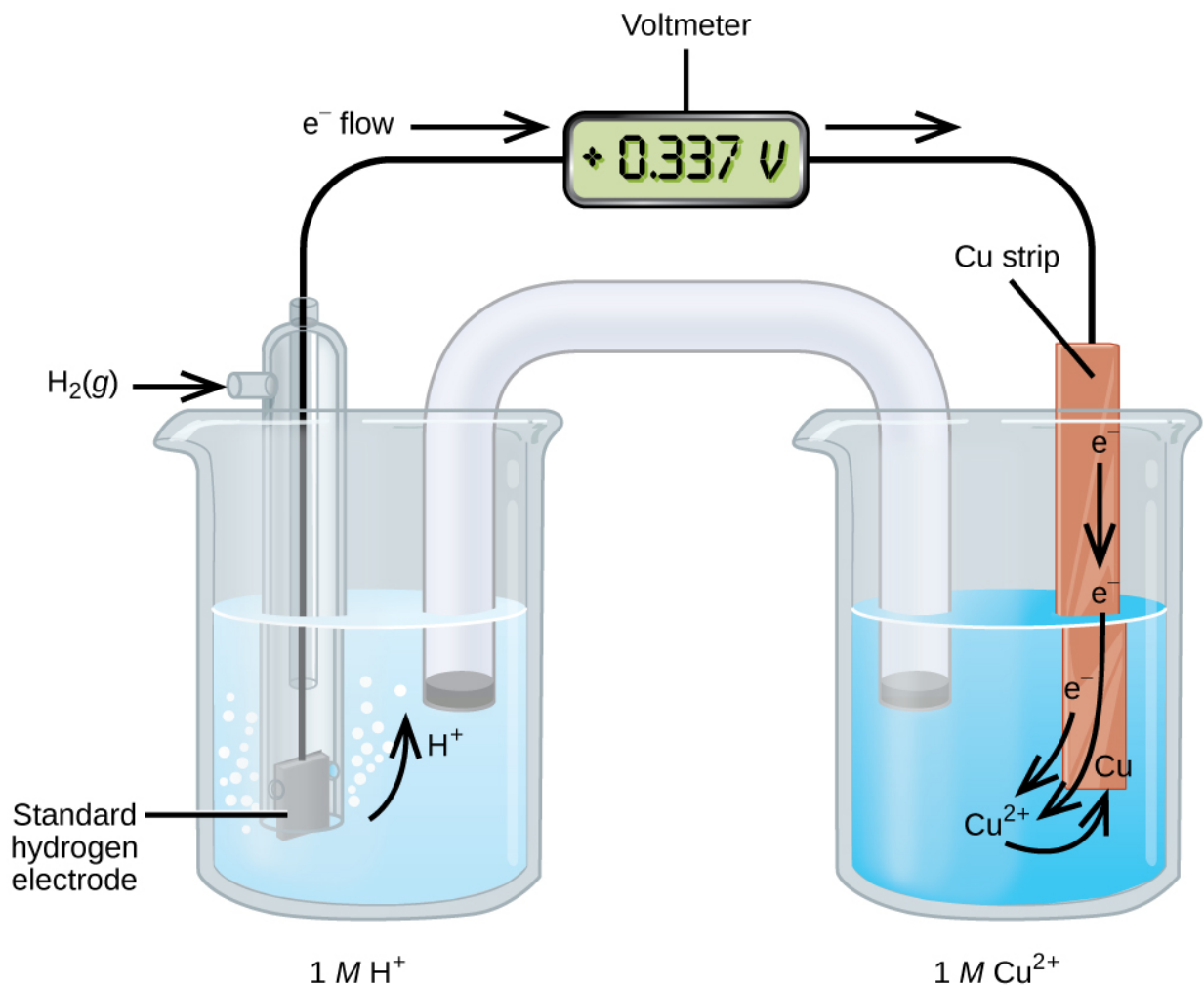
The standard cell potential, E°_{cell} , can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is necessary because oxidation is the reverse of reduction. The minus sign is necessary because oxidation is the reverse of reduction.

Equation:

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

Equation:

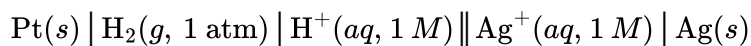
$$+0.34 \text{ V} = E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{H}^+/\text{H}_2} = E^\circ_{\text{Cu}^{2+}/\text{Cu}} - 0 = E^\circ_{\text{Cu}^{2+}/\text{Cu}}$$



A galvanic cell can be used to determine the standard reduction potential of Cu^{2+} .

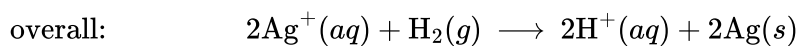
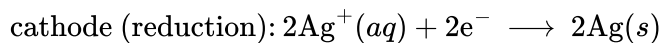
Using the SHE as a reference, other standard reduction potentials can be determined. Consider the cell shown in [link](#), where

Equation:



Electrons flow from left to right, and the reactions are

Equation:



The standard cell potential, E°_{cell} , can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is needed because oxidation is the reverse of reduction.

Equation:

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

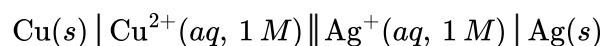
Equation:

$$+0.80 \text{ V} = E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{H}^+/\text{H}_2} = E^\circ_{\text{Ag}^+/\text{Ag}} - 0 = E^\circ_{\text{Ag}^+/\text{Ag}}$$

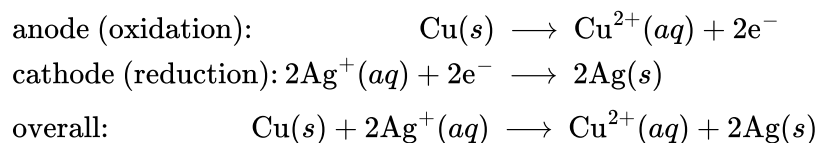
It is important to note that the potential is *not* doubled for the cathode reaction.

The SHE is rather dangerous and rarely used in the laboratory. Its main significance is that it established the zero for standard reduction potentials. Once determined, standard reduction potentials can be used to determine the **standard cell potential**, E°_{cell} , for any cell. For example, for the cell shown in [\[link\]](#),

Equation:



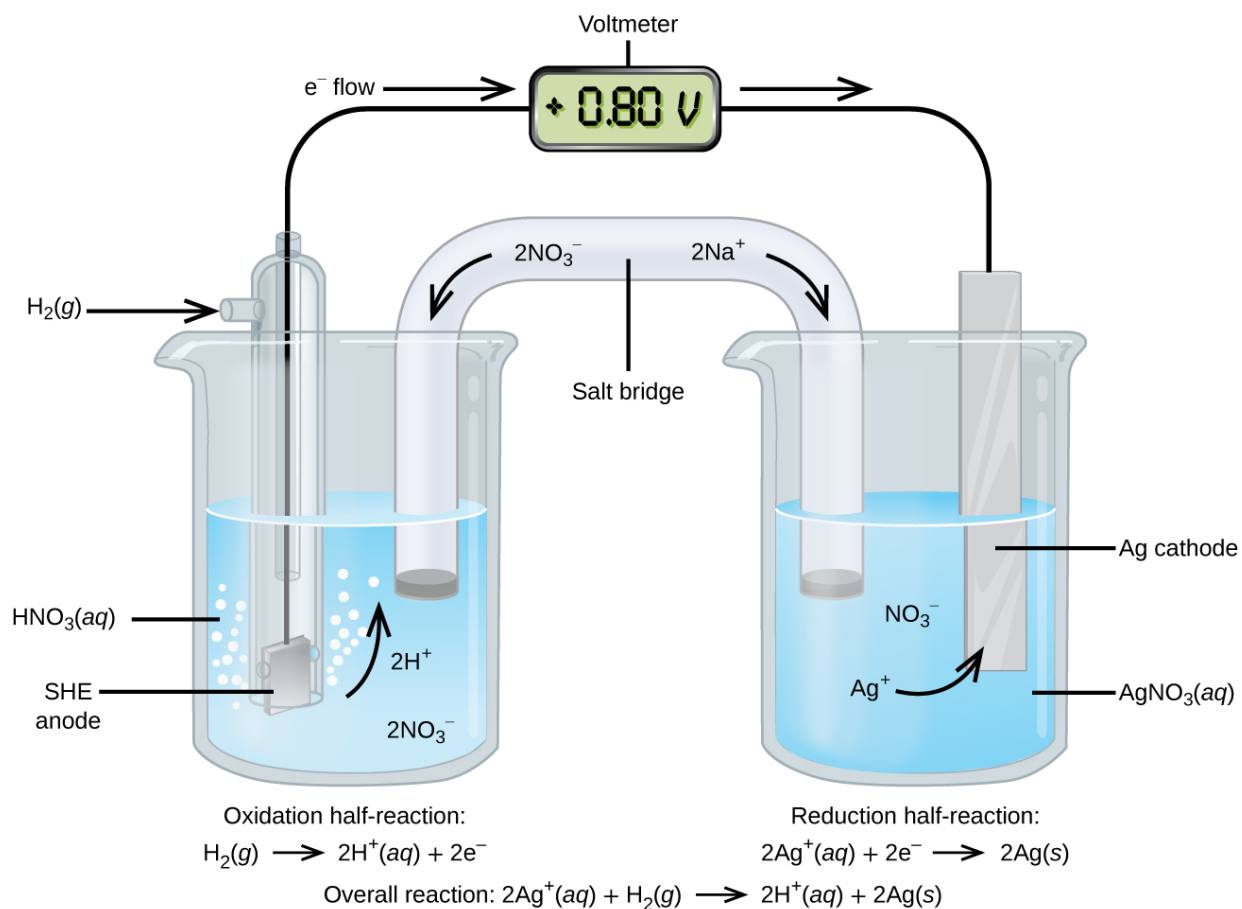
Equation:



Equation:

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.80 \text{ V} - 0.34 \text{ V} = 0.46 \text{ V}$$

Again, note that when calculating E°_{cell} , standard reduction potentials always remain the same even when a half-reaction is multiplied by a factor. Standard reduction potentials for selected reduction reactions are shown in [\[link\]](#). A more complete list is provided in [Appendix L](#).



A galvanic cell can be used to determine the standard reduction potential of Ag^+ . The SHE on the left is the anode and assigned a standard reduction potential of zero.

Selected Standard Reduction Potentials at 25 °C	
Half-Reaction	E° (V)
$\text{F}_2(\text{g}) + 2\text{e}^- \longrightarrow 2\text{F}^-(\text{aq})$	+2.866
$\text{PbO}_2(\text{s}) + \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$	+1.69
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	+1.507
$\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Au}(\text{s})$	+1.498

Selected Standard Reduction Potentials at 25 °C	
Half-Reaction	E° (V)
$\text{Cl}_2(g) + 2e^- \longrightarrow 2\text{Cl}^-(aq)$	+1.35827
$\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \longrightarrow 2\text{H}_2\text{O}(l)$	+1.229
$\text{Pt}^{2+}(aq) + 2e^- \longrightarrow \text{Pt}(s)$	+1.20
$\text{Br}_2(aq) + 2e^- \longrightarrow 2\text{Br}^-(aq)$	+1.0873
$\text{Ag}^+(aq) + e^- \longrightarrow \text{Ag}(s)$	+0.7996
$\text{Hg}_2^{2+}(aq) + 2e^- \longrightarrow 2\text{Hg}(l)$	+0.7973
$\text{Fe}^{3+}(aq) + e^- \longrightarrow \text{Fe}^{2+}(aq)$	+0.771
$\text{MnO}_4^-(aq) + 2\text{H}_2\text{O}(l) + 3e^- \longrightarrow \text{MnO}_2(s) + 4\text{OH}^-(aq)$	+0.558
$\text{I}_2(s) + 2e^- \longrightarrow 2\text{I}^-(aq)$	+0.5355
$\text{NiO}_2(s) + 2\text{H}_2\text{O}(l) + 2e^- \longrightarrow \text{Ni}(\text{OH})_2(s) + 2\text{OH}^-(aq)$	+0.49
$\text{Cu}^{2+}(aq) + 2e^- \longrightarrow \text{Cu}(s)$	+0.34
$\text{Hg}_2\text{Cl}_2(s) + 2e^- \longrightarrow 2\text{Hg}(l) + 2\text{Cl}^-(aq)$	+0.26808
$\text{AgCl}(s) + e^- \longrightarrow \text{Ag}(s) + \text{Cl}^-(aq)$	+0.22233
$\text{Sn}^{4+}(aq) + 2e^- \longrightarrow \text{Sn}^{2+}(aq)$	+0.151
$2\text{H}^+(aq) + 2e^- \longrightarrow \text{H}_2(g)$	0.00
$\text{Pb}^{2+}(aq) + 2e^- \longrightarrow \text{Pb}(s)$	-0.1262
$\text{Sn}^{2+}(aq) + 2e^- \longrightarrow \text{Sn}(s)$	-0.1375
$\text{Ni}^{2+}(aq) + 2e^- \longrightarrow \text{Ni}(s)$	-0.257
$\text{Co}^{2+}(aq) + 2e^- \longrightarrow \text{Co}(s)$	-0.28
$\text{PbSO}_4(s) + 2e^- \longrightarrow \text{Pb}(s) + \text{SO}_4^{2-}(aq)$	-0.3505
$\text{Cd}^{2+}(aq) + 2e^- \longrightarrow \text{Cd}(s)$	-0.4030
$\text{Fe}^{2+}(aq) + 2e^- \longrightarrow \text{Fe}(s)$	-0.447

Selected Standard Reduction Potentials at 25 °C	
Half-Reaction	E° (V)
$\text{Cr}^{3+}(aq) + 3e^- \longrightarrow \text{Cr}(s)$	-0.744
$\text{Mn}^{2+}(aq) + 2e^- \longrightarrow \text{Mn}(s)$	-1.185
$\text{Zn}(\text{OH})_2(s) + 2e^- \longrightarrow \text{Zn}(s) + 2\text{OH}^-(aq)$	-1.245
$\text{Zn}^{2+}(aq) + 2e^- \longrightarrow \text{Zn}(s)$	-0.7618
$\text{Al}^{3+}(aq) + 3e^- \longrightarrow \text{Al}(s)$	-1.662
$\text{Mg}^{2+}(aq) + 2e^- \longrightarrow \text{Mg}(s)$	-2.372
$\text{Na}^+(aq) + e^- \longrightarrow \text{Na}(s)$	-2.71
$\text{Ca}^{2+}(aq) + 2e^- \longrightarrow \text{Ca}(s)$	-2.868
$\text{Ba}^{2+}(aq) + 2e^- \longrightarrow \text{Ba}(s)$	-2.912
$\text{K}^+(aq) + e^- \longrightarrow \text{K}(s)$	-2.931
$\text{Li}^+(aq) + e^- \longrightarrow \text{Li}(s)$	-3.04

Tables like this make it possible to determine the standard cell potential for many oxidation-reduction reactions.

Example:

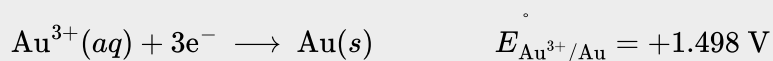
Cell Potentials from Standard Reduction Potentials

What is the standard cell potential for a galvanic cell that consists of Au^{3+}/Au and Ni^{2+}/Ni half-cells? Identify the oxidizing and reducing agents.

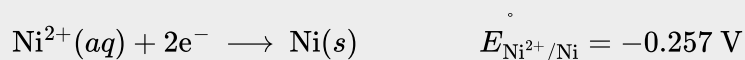
Solution

Using [\[link\]](#), the reactions involved in the galvanic cell, both written as reductions, are

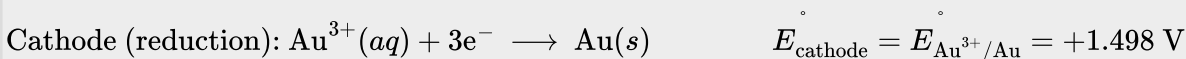
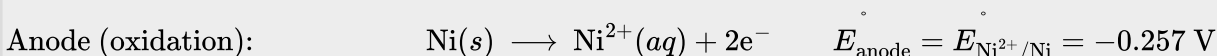
Equation:



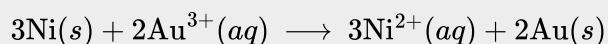
Equation:



Galvanic cells have positive cell potentials, and all the reduction reactions are reversible. The reaction at the anode will be the half-reaction with the smaller or more negative standard reduction potential. Reversing the reaction at the anode (to show the oxidation) but *not* its standard reduction potential gives:

Equation:

The least common factor is six, so the overall reaction is

Equation:

The reduction potentials are *not* scaled by the stoichiometric coefficients when calculating the cell potential, and the unmodified standard reduction potentials must be used.

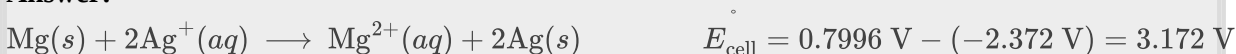
Equation:

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 1.498 \text{ V} - (-0.257 \text{ V}) = 1.755 \text{ V}$$

From the half-reactions, Ni is oxidized, so it is the reducing agent, and Au^{3+} is reduced, so it is the oxidizing agent.

Check Your Learning

A galvanic cell consists of a Mg electrode in 1 M $\text{Mg}(\text{NO}_3)_2$ solution and a Ag electrode in 1 M AgNO_3 solution. Calculate the standard cell potential at 25 °C.

Note:**Answer:****Key Concepts and Summary**

Assigning the potential of the standard hydrogen electrode (SHE) as zero volts allows the determination of standard reduction potentials, E° , for half-reactions in electrochemical cells. As the name implies, standard reduction potentials use standard states (1 bar or 1 atm for gases; 1 M for solutes, often at 298.15 K) and are written as reductions (where electrons appear on the left side of the equation). The reduction reactions are reversible, so standard cell potentials can be calculated by subtracting the standard reduction potential for the reaction at the anode from the standard reduction potential for the reaction at the cathode. When calculating the standard cell potential, the standard reduction potentials are *not* scaled by the stoichiometric coefficients in the balanced overall equation.

Key Equations

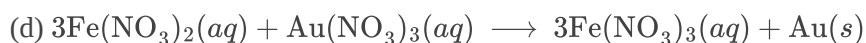
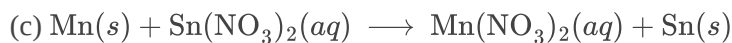
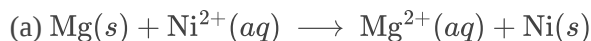
- $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$

Chemistry End of Chapter Exercises

Exercise:

Problem:

For each reaction listed, determine its standard cell potential at 25 °C and whether the reaction is spontaneous at standard conditions.



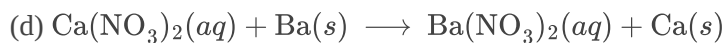
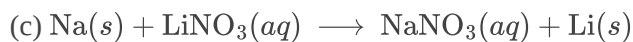
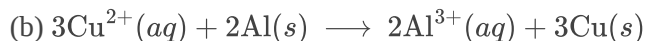
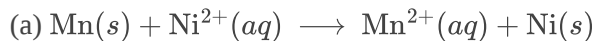
Solution:

(a) +2.115 V (spontaneous); (b) +0.4626 V (spontaneous); (c) +1.0589 V (spontaneous); (d) +0.727 V (spontaneous)

Exercise:

Problem:

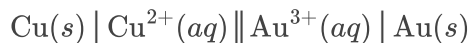
For each reaction listed, determine its standard cell potential at 25 °C and whether the reaction is spontaneous at standard conditions.



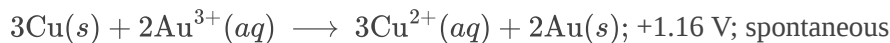
Exercise:

Problem:

Determine the overall reaction and its standard cell potential at 25 °C for this reaction. Is the reaction spontaneous at standard conditions?



Solution:



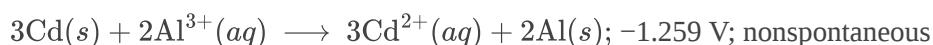
Exercise:

Problem:

Determine the overall reaction and its standard cell potential at 25 °C for the reaction involving the galvanic cell made from a half-cell consisting of a silver electrode in 1 *M* silver nitrate solution and a half-cell consisting of a zinc electrode in 1 *M* zinc nitrate. Is the reaction spontaneous at standard conditions?

Exercise:**Problem:**

Determine the overall reaction and its standard cell potential at 25 °C for the reaction involving the galvanic cell in which cadmium metal is oxidized to 1 *M* cadmium(II) ion and a half-cell consisting of an aluminum electrode in 1 *M* aluminum nitrate solution. Is the reaction spontaneous at standard conditions?

Solution:**Exercise:****Problem:**

Determine the overall reaction and its standard cell potential at 25 °C for these reactions. Is the reaction spontaneous at standard conditions? Assume the standard reduction for $\text{Br}_2(l)$ is the same as for $\text{Br}_2(aq)$.

**Glossary**

standard cell potential (E_{cell}°)

the cell potential when all reactants and products are in their standard states (1 bar or 1 atm or gases; 1 *M* for solutes), usually at 298.15 K; can be calculated by subtracting the standard reduction potential for the half-reaction at the anode from the standard reduction potential for the half-reaction occurring at the cathode

standard hydrogen electrode (SHE)

the electrode consists of hydrogen gas bubbling through hydrochloric acid over an inert platinum electrode whose reduction at standard conditions is assigned a value of 0 V; the reference point for standard reduction potentials

standard reduction potential (E°)

the value of the reduction under standard conditions (1 bar or 1 atm for gases; 1 *M* for solutes) usually at 298.15 K; tabulated values used to calculate standard cell potentials

The Nernst Equation

By the end of this section, you will be able to:

- Relate cell potentials to free energy changes
- Use the Nernst equation to determine cell potentials at nonstandard conditions
- Perform calculations that involve converting between cell potentials, free energy changes, and equilibrium constants

We will now extend electrochemistry by determining the relationship between E_{cell}° and the thermodynamics quantities such as ΔG° (Gibbs free energy) and K (the equilibrium constant). In galvanic cells, chemical energy is converted into electrical energy, which can do work. The electrical work is the product of the charge transferred multiplied by the potential difference (voltage):

Equation:

$$\text{electrical work} = \text{volts} \times (\text{charge in coulombs}) = \text{J}$$

The charge on 1 mole of electrons is given by **Faraday's constant** (F)

Equation:

$$F = \frac{6.022 \times 10^{23} \text{e}^{-}}{\text{mol}} \times \frac{1.602 \times 10^{-19} \text{C}}{\text{e}^{-}} = 9.648 \times 10^4 \frac{\text{C}}{\text{mol}} = 9.648 \times 10^4 \frac{\text{J}}{\text{V} \cdot \text{mol}}$$

Equation:

$$\text{total charge} = (\text{number of moles of e}^{-}) \times F = nF$$

In this equation, n is the number of moles of electrons for the *balanced* oxidation-reduction reaction. The measured cell potential is the maximum potential the cell can produce and is related to the **electrical work** (w_{ele}) by

Equation:

$$E_{\text{cell}} = \frac{-w_{\text{ele}}}{nF} \quad \text{or} \quad w_{\text{ele}} = -nFE_{\text{cell}}$$

The negative sign for the work indicates that the electrical work is done by the system (the galvanic cell) on the surroundings. In an earlier chapter, the free energy was defined as the energy that was available to do work. In particular, the change in free energy was defined in terms of the maximum work (w_{max}), which, for electrochemical systems, is w_{ele} .

Equation:

$$\Delta G = w_{\text{max}} = w_{\text{ele}}$$

Equation:

$$\Delta G = -nFE_{\text{cell}}$$

We can verify the signs are correct when we realize that n and F are positive constants and that galvanic cells, which have positive cell potentials, involve spontaneous reactions. Thus, spontaneous

reactions, which have $\Delta G < 0$, must have $E_{\text{cell}} > 0$. If all the reactants and products are in their standard states, this becomes

Equation:

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ$$

This provides a way to relate standard cell potentials to equilibrium constants, since

Equation:

$$\Delta G^\circ = -RT \ln K$$

Equation:

$$-nFE_{\text{cell}}^\circ = -RT \ln K \quad \text{or} \quad E_{\text{cell}}^\circ = \frac{RT}{nF} \ln K$$

Most of the time, the electrochemical reactions are run at standard temperature (298.15 K). Collecting terms at this temperature yields

Equation:

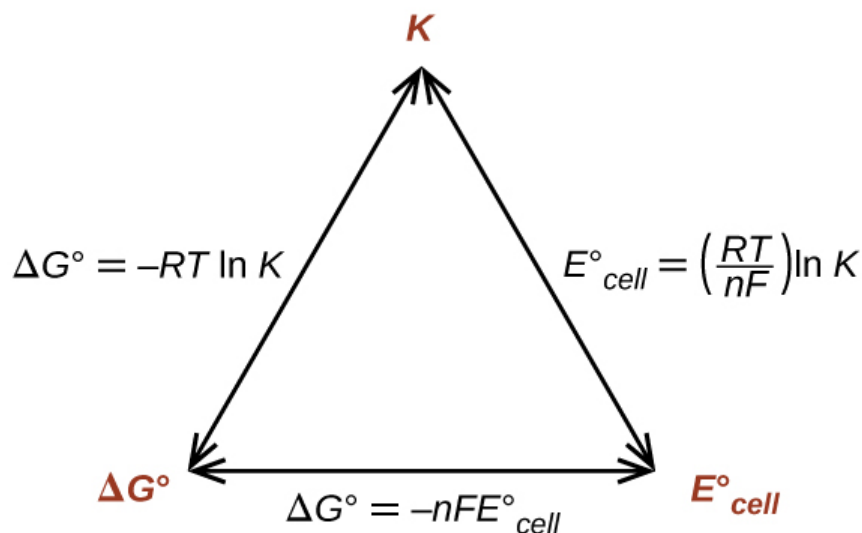
$$E_{\text{cell}}^\circ = \frac{RT}{nF} \ln K = \frac{\left(8.314 \frac{\text{J}}{\text{K}\cdot\text{mol}}\right) (298.15\text{K})}{n \times 96,485 \text{ C/V}\cdot\text{mol}} \ln K = \frac{0.0257 \text{ V}}{n} \ln K$$

where n is the number of moles of electrons. For historical reasons, the logarithm in equations involving cell potentials is often expressed using base 10 logarithms (log), which changes the constant by a factor of 2.303:

Equation:

$$E_{\text{cell}}^\circ = \frac{0.0592 \text{ V}}{n} \log K$$

Thus, if ΔG° , K , or E_{cell}° is known or can be calculated, the other two quantities can be readily determined. The relationships are shown graphically in [\[link\]](#).



The relationships between ΔG° , K , and E°_{cell} . Given any one of the three quantities, the other two can be calculated, so any of the quantities could be used to determine whether a process was spontaneous.

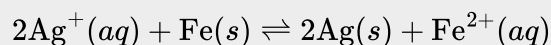
Given any one of the quantities, the other two can be calculated.

Example:

Equilibrium Constants, Standard Cell Potentials, and Standard Free Energy Changes

What is the standard free energy change and equilibrium constant for the following reaction at 25 °C?

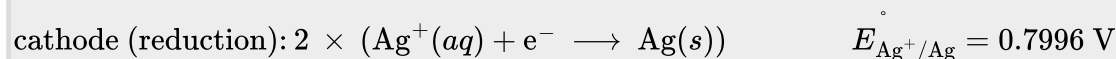
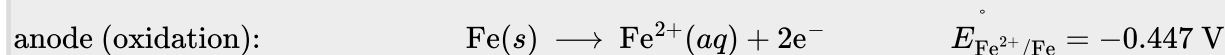
Equation:



Solution

The reaction involves an oxidation-reduction reaction, so the standard cell potential can be calculated using the data in [Appendix L](#).

Equation:



$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Fe}^{2+}/\text{Fe}} = +1.247 \text{ V}$$

Remember that the cell potential for the cathode is not multiplied by two when determining the standard cell potential. With $n = 2$, the equilibrium constant is then

Equation:

$$E_{\text{cell}}^{\circ} = \frac{0.0592 \text{ V}}{n} \log K$$

Equation:

$$K = 10^{n \times E_{\text{cell}}^{\circ} / 0.0592 \text{ V}}$$

Equation:

$$K = 10^{2 \times 1.247 \text{ V} / 0.0592 \text{ V}}$$

Equation:

$$K = 10^{42.128}$$

Equation:

$$K = 1.3 \times 10^{42}$$

The standard free energy is then

Equation:

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$$

Equation:

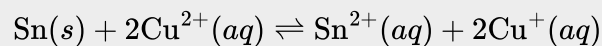
$$\Delta G^{\circ} = -2 \times 96,485 \frac{\text{J}}{\text{V} \cdot \text{mol}} \times 1.247 \text{ V} = -240.6 \frac{\text{kJ}}{\text{mol}}$$

Check your answer: A positive standard cell potential means a spontaneous reaction, so the standard free energy change should be negative, and an equilibrium constant should be >1 .

Check Your Learning

What is the standard free energy change and the equilibrium constant for the following reaction at room temperature? Is the reaction spontaneous?

Equation:



Note:

Answer:

Spontaneous; $n = 2$; $E_{\text{cell}}^{\circ} = +0.291 \text{ V}$; $\Delta G^{\circ} = -56.2 \frac{\text{kJ}}{\text{mol}}$; $K = 6.8 \times 10^9$.

Now that the connection has been made between the free energy and cell potentials, nonstandard concentrations follow. Recall that

Equation:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

where Q is the reaction quotient (see the chapter on equilibrium fundamentals). Converting to cell potentials:

Equation:

$$-nFE_{\text{cell}} = -nFE_{\text{cell}}^\circ + RT \ln Q \quad \text{or} \quad E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln Q$$

This is the **Nernst equation**. At standard temperature (298.15 K), it is possible to write the above equations as

Equation:

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0257 \text{ V}}{n} \ln Q \quad \text{or} \quad E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592 \text{ V}}{n} \log Q$$

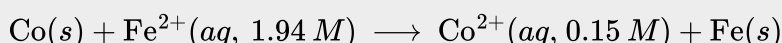
If the temperature is not 298.15 K, it is necessary to recalculate the value of the constant. With the Nernst equation, it is possible to calculate the cell potential at nonstandard conditions. This adjustment is necessary because potentials determined under different conditions will have different values.

Example:

Cell Potentials at Nonstandard Conditions

Consider the following reaction at room temperature:

Equation:



Is the process spontaneous?

Solution

There are two ways to solve the problem. If the thermodynamic information in [Appendix G](#) were available, you could calculate the free energy change. If the free energy change is negative, the process is spontaneous. The other approach, which we will use, requires information like that given in [Appendix L](#). Using those data, the cell potential can be determined. If the cell potential is positive, the process is spontaneous. Collecting information from [Appendix L](#) and the problem,

Equation:



$$E_{\text{cell}} = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = -0.447 \text{ V} - (-0.28 \text{ V}) = -0.17 \text{ V}$$

The process is not spontaneous under standard conditions. Using the Nernst equation and the concentrations stated in the problem and $n = 2$,

Equation:

$$Q = \frac{[\text{Co}^{2+}]}{[\text{Fe}^{2+}]} = \frac{0.15\text{ M}}{1.94\text{ M}} = 0.077$$

Equation:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592\text{ V}}{n} \log Q$$

Equation:

$$E_{\text{cell}} = -0.17\text{ V} - \frac{0.0592\text{ V}}{2} \log 0.077$$

Equation:

$$E_{\text{cell}} = -0.17\text{ V} + 0.033\text{ V} = -0.014\text{ V}$$

The process is (still) nonspontaneous.

Check Your Learning

What is the cell potential for the following reaction at room temperature?

Equation:



What are the values of n and Q for the overall reaction? Is the reaction spontaneous under these conditions?

Note:

Answer:

$n = 6$; $Q = 1440$; $E_{\text{cell}} = +1.97\text{ V}$, spontaneous.

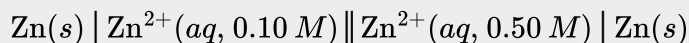
Finally, we will take a brief look at a special type of cell called a **concentration cell**. In a concentration cell, the electrodes are the same material and the half-cells differ only in concentration. Since one or both compartments is not standard, the cell potentials will be unequal; therefore, there will be a potential difference, which can be determined with the aid of the Nernst equation.

Example:

Concentration Cells

What is the cell potential of the concentration cell described by

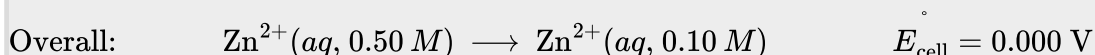
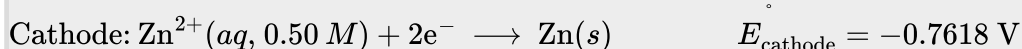
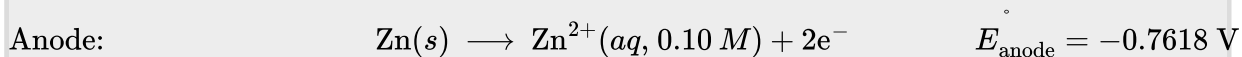
Equation:



Solution

From the information given:

Equation:



The standard cell potential is zero because the anode and cathode involve the same reaction; only the concentration of Zn^{2+} changes. Substituting into the Nernst equation,

Equation:

$$E_{\text{cell}} = 0.000\text{ V} - \frac{0.0592\text{ V}}{2} \log \frac{0.10}{0.50} = +0.021\text{ V}$$

and the process is spontaneous at these conditions.

Check your answer: In a concentration cell, the standard cell potential will always be zero. To get a positive cell potential (spontaneous process) the reaction quotient Q must be <1 . $Q < 1$ in this case, so the process is spontaneous.

Check Your Learning

What value of Q for the previous concentration cell would result in a voltage of 0.10 V ? If the concentration of zinc ion at the cathode was 0.50 M , what was the concentration at the anode?

Note:

Answer:

$$Q = 0.00042; [\text{Zn}^{2+}]_{\text{cat}} = 2.1 \times 10^{-4}\text{ M}.$$

Key Concepts and Summary

Electrical work (w_{ele}) is the negative of the product of the total charge (Q) and the cell potential (E_{cell}). The total charge can be calculated as the number of moles of electrons (n) times the Faraday constant ($F = 96,485\text{ C/mol e}^{-}$). Electrical work is the maximum work that the system can produce and so is equal to the change in free energy. Thus, anything that can be done with or to a free energy change can also be done to or with a cell potential. The Nernst equation relates the cell potential at nonstandard conditions to the logarithm of the reaction quotient. Concentration cells exploit this relationship and produce a positive cell potential using half-cells that differ only in the concentration of their solutes.

Key Equations

- $E_{\text{cell}}^{\circ} = \frac{RT}{nF} \ln K$
- $E_{\text{cell}}^{\circ} = \frac{0.0257 \text{ V}}{n} \ln K = \frac{0.0592 \text{ V}}{n} \log K$ (at 298.15 K)
- $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln Q$ (Nernst equation)
- $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0257 \text{ V}}{n} \ln Q = E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log Q$ (at 298.15 K)
- $\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$
- $w_{\text{ele}} = w_{\text{max}} = -nFE_{\text{cell}}$

Chemistry End of Chapter Exercises

Exercise:

Problem: For the standard cell potentials given here, determine the ΔG° for the cell in kJ.

(a) 0.000 V, $n = 2$

(b) +0.434 V, $n = 2$

(c) -2.439 V, $n = 1$

Solution:

(a) 0 kJ/mol; (b) -83.7 kJ/mol; (c) +235.3 kJ/mol

Exercise:

Problem: For the ΔG° values given here, determine the standard cell potential for the cell.

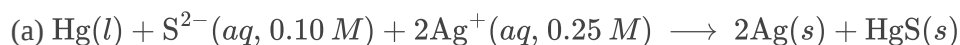
(a) 12 kJ/mol, $n = 3$

(b) -45 kJ/mol, $n = 1$

Exercise:

Problem:

Determine the standard cell potential and the cell potential under the stated conditions for the electrochemical reactions described here. State whether each is spontaneous or nonspontaneous under each set of conditions at 298.15 K.



(b) The galvanic cell made from a half-cell consisting of an aluminum electrode in 0.015 M aluminum nitrate solution and a half-cell consisting of a nickel electrode in 0.25 M nickel(II) nitrate solution.

(c) The cell made of a half-cell in which 1.0 *M* aqueous bromide is oxidized to 0.11 *M* bromine ion and a half-cell in which aluminum ion at 0.023 *M* is reduced to aluminum metal. Assume the standard reduction potential for Br₂(l) is the same as that of Br₂(aq).

Solution:

(a) standard cell potential: 1.50 V, spontaneous; cell potential under stated conditions: 1.43 V, spontaneous; (b) standard cell potential: 1.405 V, spontaneous; cell potential under stated conditions: 1.423 V, spontaneous; (c) standard cell potential: -2.749 V, nonspontaneous; cell potential under stated conditions: -2.757 V, nonspontaneous

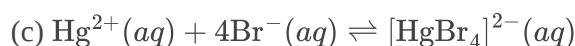
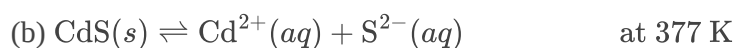
Exercise:

Problem: Determine ΔG and ΔG° for each of the reactions in the previous problem.

Exercise:

Problem:

Use the data in [Appendix L](#) to determine the equilibrium constant for the following reactions. Assume 298.15 K if no temperature is given.



Solution:

(a) 1.7×10^{-10} ; (b) 2.6×10^{-21} ; (c) 8.9×10^{19} ; (d) 1.0×10^{-14}

Glossary

concentration cell

galvanic cell in which the two half-cells are the same except for the concentration of the solutes; spontaneous when the overall reaction is the dilution of the solute

electrical work (w_{ele})

negative of total charge times the cell potential; equal to w_{max} for the system, and so equals the free energy change (ΔG)

Faraday's constant (*F*)

charge on 1 mol of electrons; $F = 96,485 \text{ C/mol e}^-$

Nernst equation

equation that relates the logarithm of the reaction quotient (*Q*) to nonstandard cell potentials; can be used to relate equilibrium constants to standard cell potentials

Batteries and Fuel Cells

By the end of this section, you will be able to:

- Classify batteries as primary or secondary
- List some of the characteristics and limitations of batteries
- Provide a general description of a fuel cell

A **battery** is an electrochemical cell or series of cells that produces an electric current. In principle, any galvanic cell could be used as a battery. An ideal battery would never run down, produce an unchanging voltage, and be capable of withstanding environmental extremes of heat and humidity. Real batteries strike a balance between ideal characteristics and practical limitations. For example, the mass of a car battery is about 18 kg or about 1% of the mass of an average car or light-duty truck. This type of battery would supply nearly unlimited energy if used in a smartphone, but would be rejected for this application because of its mass. Thus, no single battery is “best” and batteries are selected for a particular application, keeping things like the mass of the battery, its cost, reliability, and current capacity in mind. There are two basic types of batteries: primary and secondary. A few batteries of each type are described next.

Note:



Visit this [site](#) to learn more about batteries.

Primary Batteries

Primary batteries are single-use batteries because they cannot be recharged. A common primary battery is the **dry cell** ([link](#)). The dry cell is a zinc-carbon battery. The zinc can serves as both a container and the negative electrode. The positive electrode is a rod made of carbon that is surrounded by a paste of manganese(IV) oxide, zinc chloride, ammonium chloride, carbon powder, and a small amount of water. The reaction at the anode can be represented as the ordinary oxidation of zinc:

Equation:

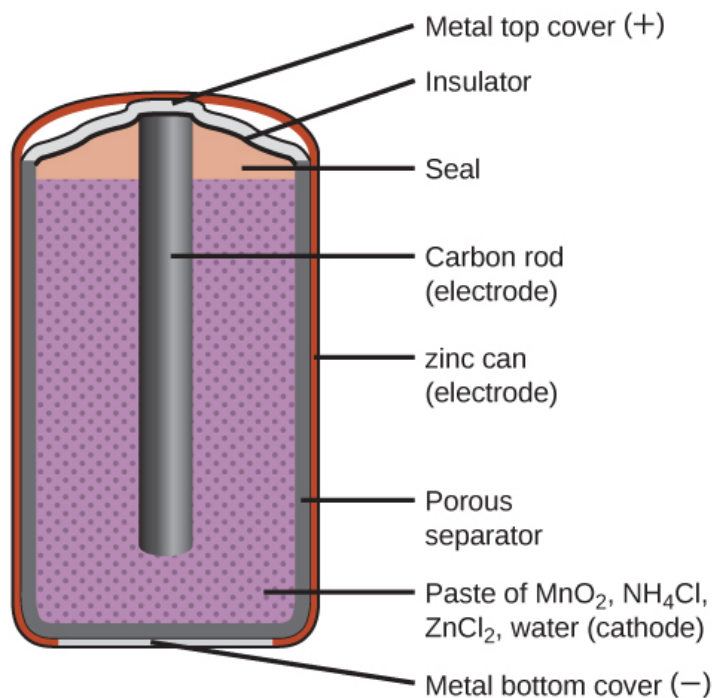


The reaction at the cathode is more complicated, in part because more than one reaction occurs. The series of reactions that occurs at the cathode is approximately

Equation:



The overall reaction for the zinc–carbon battery can be represented as $2\text{MnO}_2(s) + 2\text{NH}_4\text{Cl}(aq) + \text{Zn}(s) \longrightarrow \text{Zn}^{2+}(aq) + \text{Mn}_2\text{O}_3(s) + 2\text{NH}_3(aq) + \text{H}_2\text{O}(l) + 2\text{Cl}^-$ with an overall cell potential which is initially about 1.5 V, but decreases as the battery is used. It is important to remember that the voltage delivered by a battery is the same regardless of the size of a battery. For this reason, D, C, A, AA, and AAA batteries all have the same voltage rating. However, larger batteries can deliver more moles of electrons. As the zinc container oxidizes, its contents eventually leak out, so this type of battery should not be left in any electrical device for extended periods.



The diagram shows a cross section of a flashlight battery, a zinc-carbon dry cell.

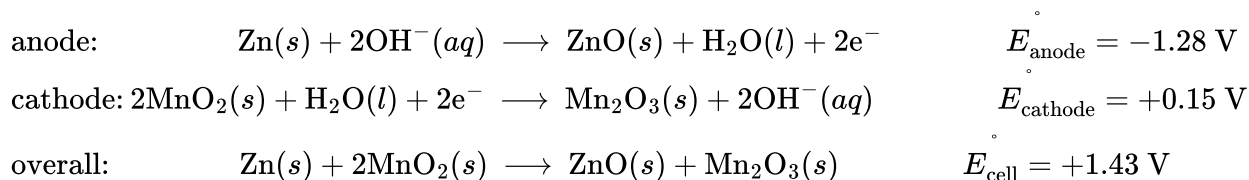
Note:



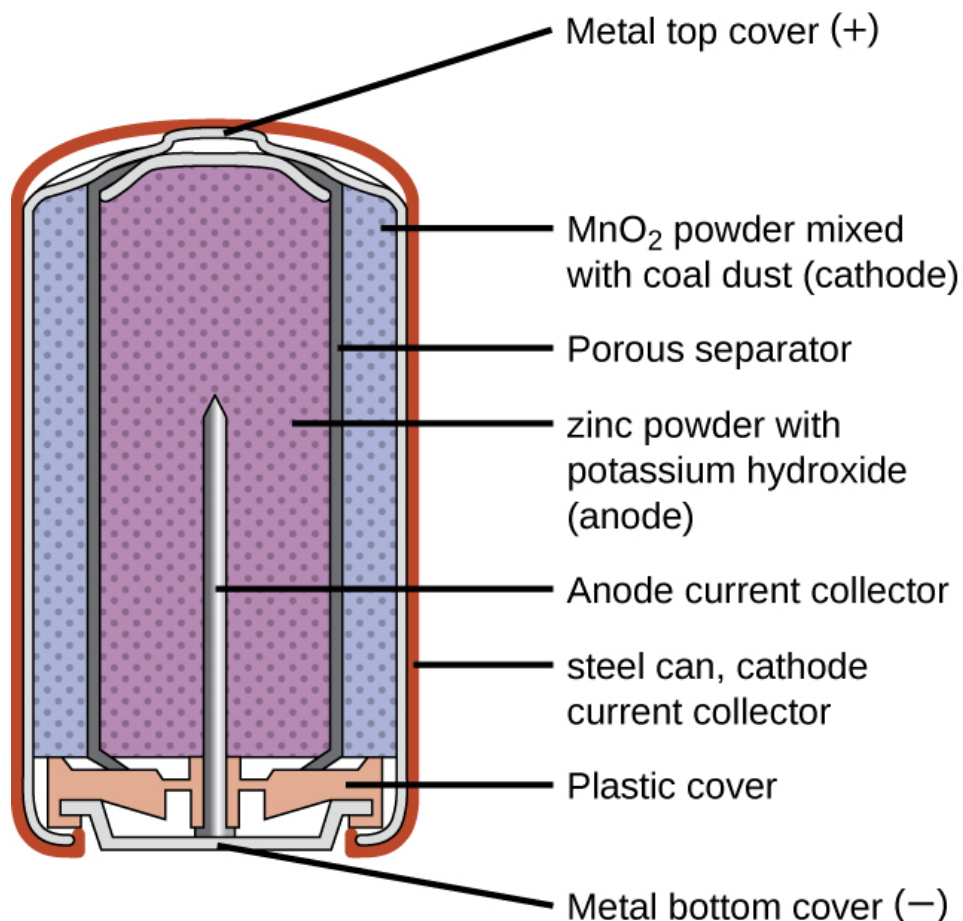
Visit this [site](#) to learn more about zinc-carbon batteries.

Alkaline batteries ([link](#)) were developed in the 1950s partly to address some of the performance issues with zinc–carbon dry cells. They are manufactured to be exact replacements for zinc-carbon dry cells. As their name suggests, these types of batteries use alkaline electrolytes, often potassium hydroxide. The reactions are

Equation:



An alkaline battery can deliver about three to five times the energy of a zinc-carbon dry cell of similar size. Alkaline batteries are prone to leaking potassium hydroxide, so these should also be removed from devices for long-term storage. While some alkaline batteries are rechargeable, most are not. Attempts to recharge an alkaline battery that is not rechargeable often leads to rupture of the battery and leakage of the potassium hydroxide electrolyte.



Alkaline batteries were designed as direct replacements for zinc-carbon

(dry cell) batteries.

Note:



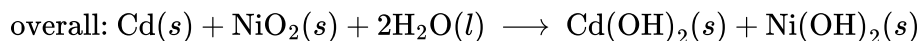
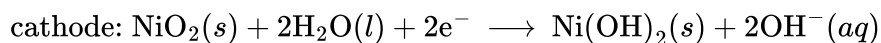
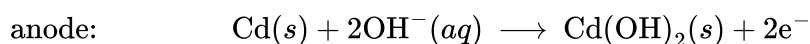
Visit this [site](#) to learn more about alkaline batteries.

Secondary Batteries

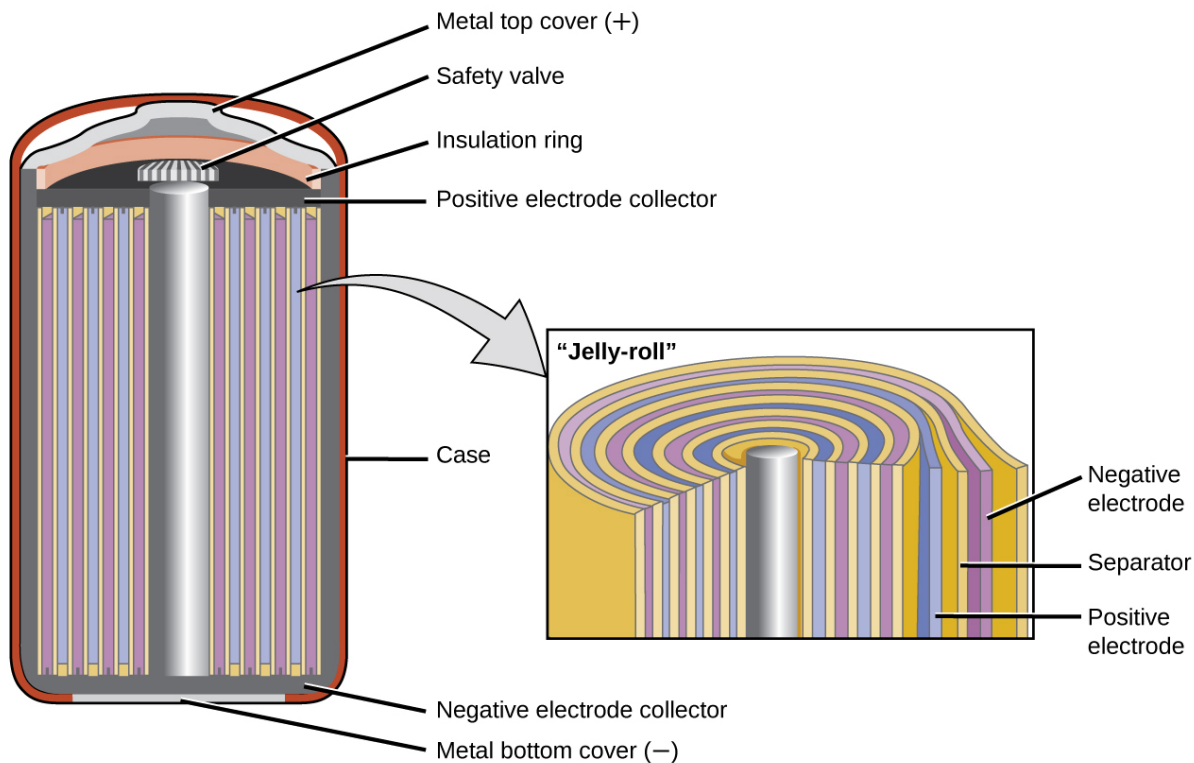
Secondary batteries are rechargeable. These are the types of batteries found in devices such as smartphones, electronic tablets, and automobiles.

Nickel-cadmium, or NiCd, batteries ([link](#)) consist of a nickel-plated cathode, cadmium-plated anode, and a potassium hydroxide electrolyte. The positive and negative plates, which are prevented from shorting by the separator, are rolled together and put into the case. This is a “jelly-roll” design and allows the NiCd cell to deliver much more current than a similar-sized alkaline battery. The reactions are

Equation:



The voltage is about 1.2 V to 1.25 V as the battery discharges. When properly treated, a NiCd battery can be recharged about 1000 times. Cadmium is a toxic heavy metal so NiCd batteries should never be opened or put into the regular trash.



NiCd batteries use a “jelly-roll” design that significantly increases the amount of current the battery can deliver as compared to a similar-sized alkaline battery.

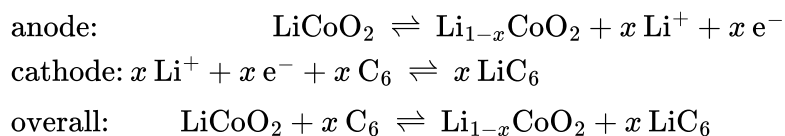
Note:



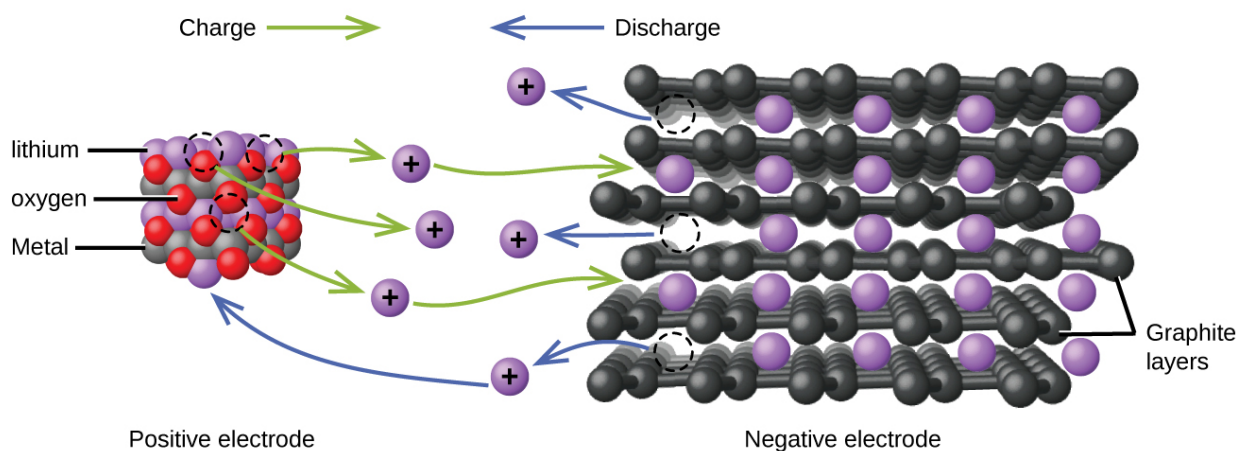
Visit this [site](#) for more information about nickel cadmium rechargeable batteries.

Lithium ion batteries ([link](#)) are among the most popular rechargeable batteries and are used in many portable electronic devices. The reactions are

Equation:



With the coefficients representing moles, x is no more than about 0.5 moles. The battery voltage is about 3.7 V. Lithium batteries are popular because they can provide a large amount current, are lighter than comparable batteries of other types, produce a nearly constant voltage as they discharge, and only slowly lose their charge when stored.



In a lithium ion battery, charge flows between the electrodes as the lithium ions move between the anode and cathode.

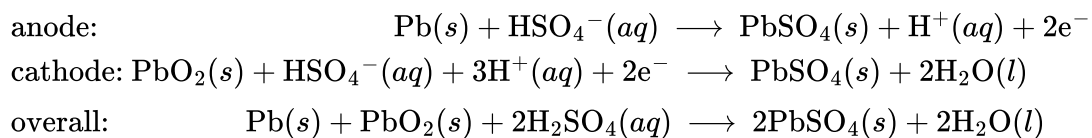
Note:



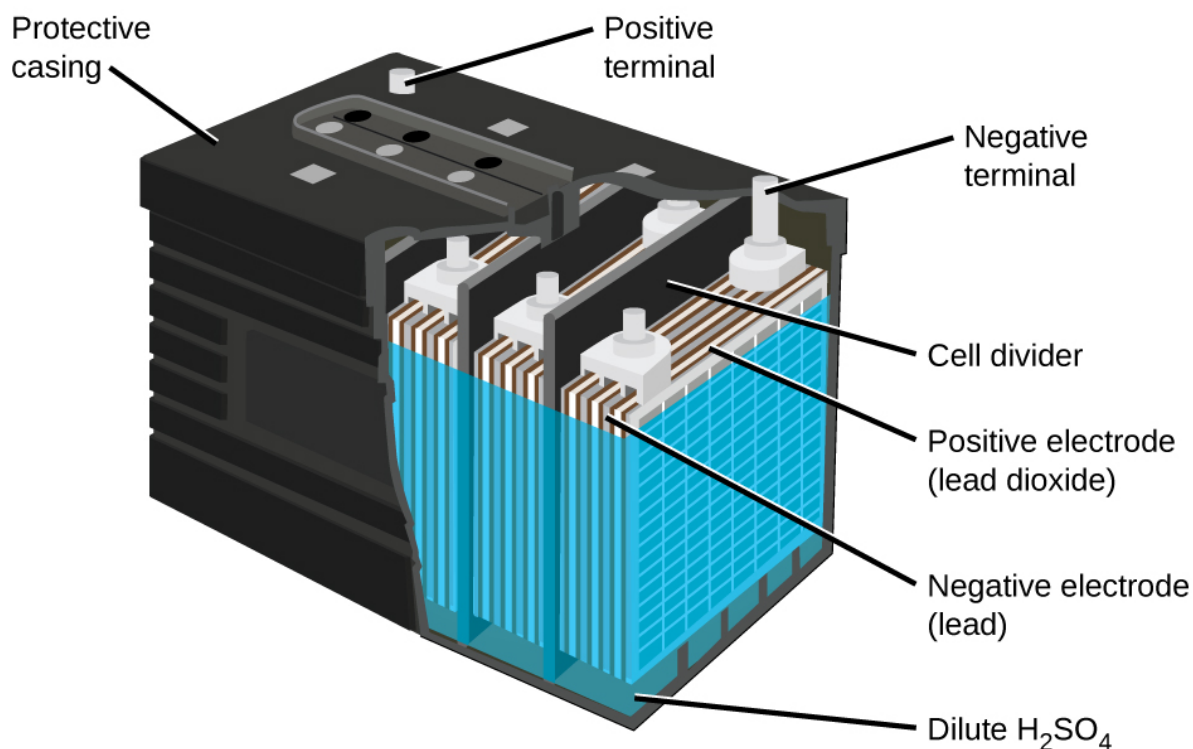
Visit this [site](#) for more information about lithium ion batteries.

The **lead acid battery** ([link](#)) is the type of secondary battery used in your automobile. It is inexpensive and capable of producing the high current required by automobile starter motors. The reactions for a lead acid battery are

Equation:



Each cell produces 2 V, so six cells are connected in series to produce a 12-V car battery. Lead acid batteries are heavy and contain a caustic liquid electrolyte, but are often still the battery of choice because of their high current density. Since these batteries contain a significant amount of lead, they must always be disposed of properly.



The lead acid battery in your automobile consists of six cells connected in series to give 12 V. Their low cost and high current output makes these excellent candidates for providing power for automobile starter motors.

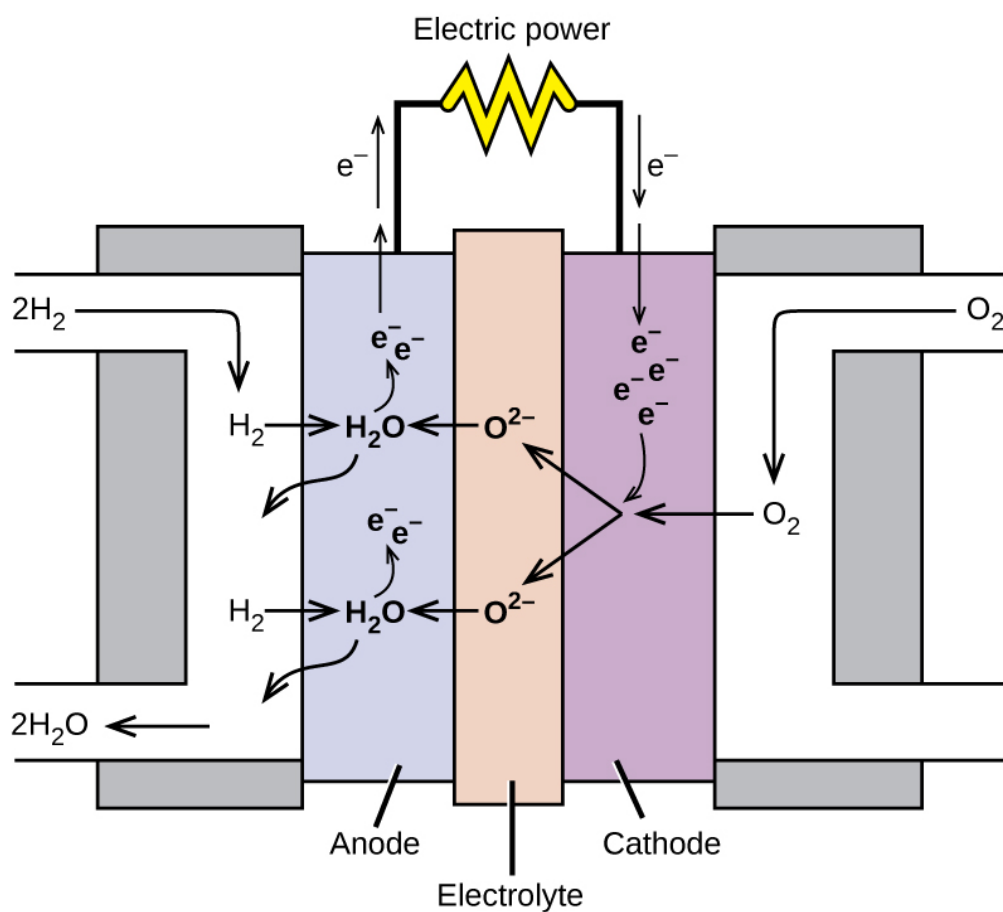
Note:



Visit this [site](#) for more information about lead acid batteries.

Fuel Cells

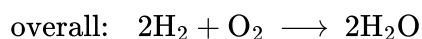
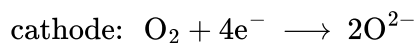
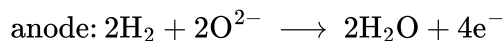
A **fuel cell** is a device that converts chemical energy into electrical energy. Fuel cells are similar to batteries but require a continuous source of fuel, often hydrogen. They will continue to produce electricity as long as fuel is available. Hydrogen fuel cells have been used to supply power for satellites, space capsules, automobiles, boats, and submarines ([link](#)).



In this hydrogen fuel-cell schematic, oxygen from the air reacts with hydrogen, producing water and electricity.

In a hydrogen fuel cell, the reactions are

Equation:



The voltage is about 0.9 V. The efficiency of fuel cells is typically about 40% to 60%, which is higher than the typical internal combustion engine (25% to 35%) and, in the case of the hydrogen fuel cell, produces only water as exhaust. Currently, fuel cells are rather expensive and contain features that cause them to fail after a relatively short time.

Note:



Check out this [link](#) to learn more about fuel cells.

Key Concepts and Summary

Batteries are galvanic cells, or a series of cells, that produce an electric current. When cells are combined into batteries, the potential of the battery is an integer multiple of the potential of a single cell. There are two basic types of batteries: primary and secondary. Primary batteries are “single use” and cannot be recharged. Dry cells and (most) alkaline batteries are examples of primary batteries. The second type is rechargeable and is called a secondary battery. Examples of secondary batteries include nickel-cadmium (NiCd), lead acid, and lithium ion batteries. Fuel cells are similar to batteries in that they generate an electrical current, but require continuous addition of fuel and oxidizer. The hydrogen fuel cell uses hydrogen and oxygen from the air to produce water, and is generally more efficient than internal combustion engines.

Chemistry End of Chapter Exercises

Exercise:

Problem: What are the desirable qualities of an electric battery?

Exercise:

Problem:

List some things that are typically considered when selecting a battery for a new application.

Solution:

Considerations include: cost of the materials used in the battery, toxicity of the various components (what constitutes proper disposal), should it be a primary or secondary battery, energy requirements (the “size” of the battery/how long should it last), will a particular battery leak when the new device is used according to directions, and its mass (the total mass of the new device).

Exercise:**Problem:**

Consider a battery made from one half-cell that consists of a copper electrode in 1 M CuSO₄ solution and another half-cell that consists of a lead electrode in 1 M Pb(NO₃)₂ solution.

- What are the reactions at the anode, cathode, and the overall reaction?
- What is the standard cell potential for the battery?
- Most devices designed to use dry-cell batteries can operate between 1.0 and 1.5 V. Could this cell be used to make a battery that could replace a dry-cell battery? Why or why not.
- Suppose sulfuric acid is added to the half-cell with the lead electrode and some PbSO₄(s) forms. Would the cell potential increase, decrease, or remain the same?

Exercise:**Problem:**

Consider a battery with the overall reaction: $\text{Cu}(s) + 2\text{Ag}^+(aq) \longrightarrow 2\text{Ag}(s) + \text{Cu}^{2+}(aq)$.

- What is the reaction at the anode and cathode?
 - A battery is “dead” when it has no cell potential. What is the value of Q when this battery is dead?
 - If a particular dead battery was found to have $[\text{Cu}^{2+}] = 0.11 \text{ M}$, what was the concentration of silver ion?
-

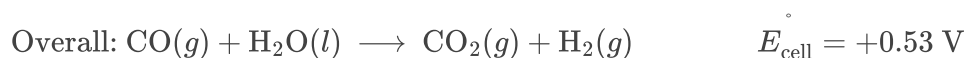
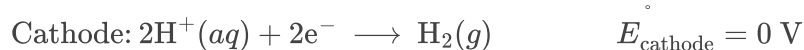
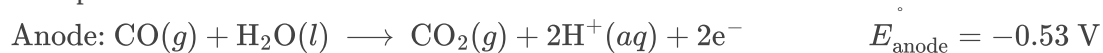
Solution:

- $$\begin{array}{ll} \text{(a) anode: } \text{Cu}(s) \longrightarrow \text{Cu}^{2+}(aq) + 2e^- & E_{\text{anode}}^\circ = 0.34 \text{ V} \\ \text{cathode: } 2 \times (\text{Ag}^+(aq) + e^- \longrightarrow \text{Ag}(s)) & E_{\text{cathode}}^\circ = 0.7996 \text{ V} \end{array}$$
- 10¹⁵; (c) $5.6 \times 10^{-9} \text{ M}$; (b) 3.5×10^{15}

Exercise:

Problem:

An inventor proposes using a SHE (standard hydrogen electrode) in a new battery for smartphones that also removes toxic carbon monoxide from the air:



Would this make a good battery for smartphones? Why or why not?

Exercise:

Problem: Why do batteries go dead, but fuel cells do not?

Solution:

Batteries are self-contained and have a limited supply of reagents to expend before going dead. Alternatively, battery reaction byproducts accumulate and interfere with the reaction. Because a fuel cell is constantly resupplied with reactants and products are expelled, it can continue to function as long as reagents are supplied.

Exercise:**Problem:**

Explain what happens to battery voltage as a battery is used, in terms of the Nernst equation.

Exercise:**Problem:**

Using the information thus far in this chapter, explain why battery-powered electronics perform poorly in low temperatures.

Solution:

E_{cell} , as described in the Nernst equation, has a term that is directly proportional to temperature. At low temperatures, this term is decreased, resulting in a lower cell voltage provided by the battery to the device—the same effect as a battery running dead.

Glossary**alkaline battery**

primary battery that uses an alkaline (often potassium hydroxide) electrolyte; designed to be an exact replacement for the dry cell, but with more energy storage and less electrolyte leakage than typical dry cell

battery

galvanic cell or series of cells that produces a current; in theory, any galvanic cell

dry cell

primary battery, also called a zinc-carbon battery; can be used in any orientation because it uses a paste as the electrolyte; tends to leak electrolyte when stored

fuel cell

devices that produce an electrical current as long as fuel and oxidizer are continuously added; more efficient than internal combustion engines

lead acid battery

secondary battery that consists of multiple cells; the lead acid battery found in automobiles has six cells and a voltage of 12 V

lithium ion battery

very popular secondary battery; uses lithium ions to conduct current and is light, rechargeable, and produces a nearly constant potential as it discharges

nickel-cadmium battery

(NiCd battery) secondary battery that uses cadmium, which is a toxic heavy metal; heavier than lithium ion batteries, but with similar performance characteristics

primary battery

single-use nonrechargeable battery

secondary battery

battery that can be recharged

Corrosion

By the end of this section, you will be able to:

- Define corrosion
- List some of the methods used to prevent or slow corrosion

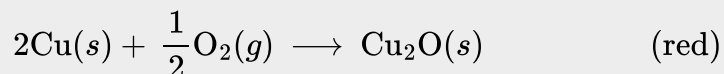
Corrosion is usually defined as the degradation of metals due to an electrochemical process. The formation of rust on iron, tarnish on silver, and the blue-green patina that develops on copper are all examples of corrosion. The total cost of corrosion in the United States is significant, with estimates in excess of half a trillion dollars a year.

Note:

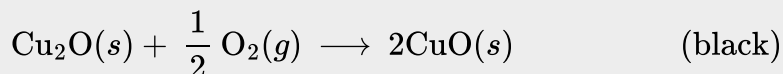
Statue of Liberty: Changing Colors

The Statue of Liberty is a landmark every American recognizes. The Statue of Liberty is easily identified by its height, stance, and unique blue-green color ([link](#)). When this statue was first delivered from France, its appearance was not green. It was brown, the color of its copper “skin.” So how did the Statue of Liberty change colors? The change in appearance was a direct result of corrosion. The copper that is the primary component of the statue slowly underwent oxidation from the air. The oxidation-reduction reactions of copper metal in the environment occur in several steps. Copper metal is oxidized to copper(I) oxide (Cu_2O), which is red, and then to copper(II) oxide, which is black

Equation:



Equation:



Coal, which was often high in sulfur, was burned extensively in the early part of the last century. As a result, sulfur trioxide, carbon dioxide, and water all reacted with the CuO

Equation:



Equation:



Equation:



These three compounds are responsible for the characteristic blue-green patina seen today. Fortunately, formation of the patina created a protective layer on the surface, preventing

further corrosion of the copper skin. The formation of the protective layer is a form of passivation, which is discussed further in a later chapter.



(a)

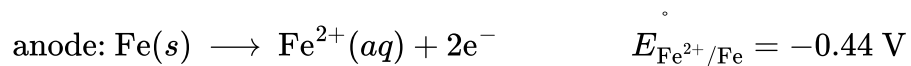


(b)

(a) The Statue of Liberty is covered with a copper skin, and was originally brown, as shown in this painting. (b) Exposure to the elements has resulted in the formation of the blue-green patina seen today.

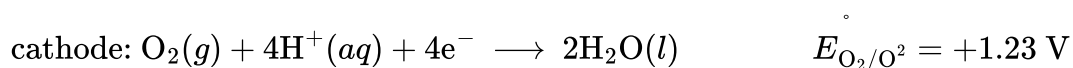
Perhaps the most familiar example of corrosion is the formation of rust on iron. Iron will rust when it is exposed to oxygen and water. The main steps in the rusting of iron appear to involve the following ([link](#)). Once exposed to the atmosphere, iron rapidly oxidizes.

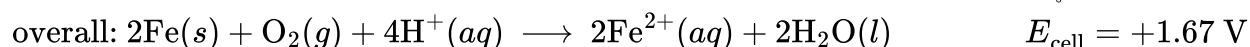
Equation:



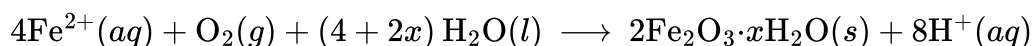
The electrons reduce oxygen in the air in acidic solutions.

Equation:

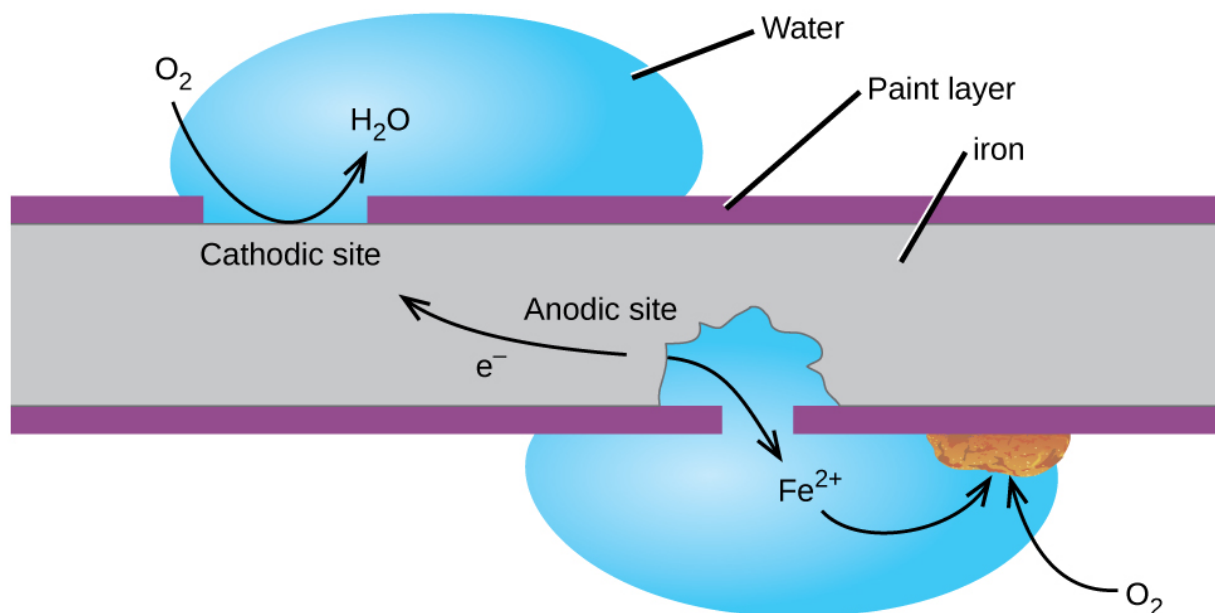


Equation:

What we call rust is hydrated iron(III) oxide, which forms when iron(II) ions react further with oxygen.

Equation:

The number of water molecules is variable, so it is represented by x . Unlike the patina on copper, the formation of rust does not create a protective layer and so corrosion of the iron continues as the rust flakes off and exposes fresh iron to the atmosphere.



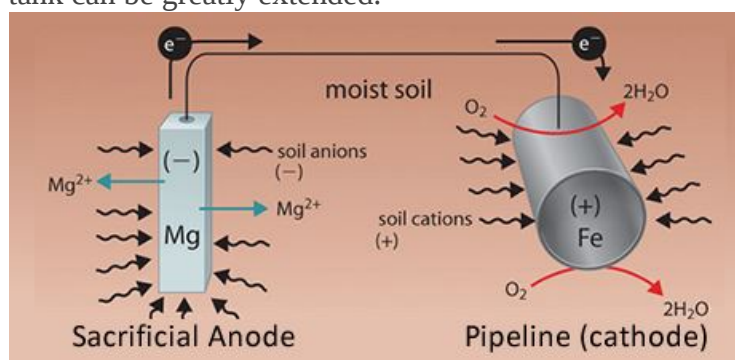
Once the paint is scratched on a painted iron surface, corrosion occurs and rust begins to form. The speed of the spontaneous reaction is increased in the presence of electrolytes, such as the sodium chloride used on roads to melt ice and snow or in salt water.

One way to keep iron from corroding is to keep it painted. The layer of paint prevents the water and oxygen necessary for rust formation from coming into contact with the iron. As long as the paint remains intact, the iron is protected from corrosion.

Other strategies include alloying the iron with other metals. For example, stainless steel is mostly iron with a bit of chromium. The chromium tends to collect near the surface, where it forms an oxide layer that protects the iron.

Zinc-plated or **galvanized iron** uses a different strategy. Zinc is more easily oxidized than iron because zinc has a lower reduction potential. Since zinc has a lower reduction potential, it is a more active metal. Thus, even if the zinc coating is scratched, the zinc will still oxidize before the iron. This suggests that this approach should work with other active metals.

Another important way to protect metal is to make it the cathode in a galvanic cell. This is **cathodic protection** and can be used for metals other than just iron. For example, the rusting of underground iron storage tanks and pipes can be prevented or greatly reduced by connecting them to a more active metal such as zinc or magnesium ([\[link\]](#)). This is also used to protect the metal parts in water heaters. The more active metals (lower reduction potential) are called **sacrificial anodes** because as they get used up as they corrode (oxidize) at the anode. The metal being protected serves as the cathode, and so does not oxidize (corrode). When the anodes are properly monitored and periodically replaced, the useful lifetime of the iron storage tank can be greatly extended.



One way to protect an underground iron storage tank is through cathodic protection. Using an active metal like zinc or magnesium for the anode effectively makes the storage tank the cathode, preventing it from corroding (oxidizing).

Key Concepts and Summary

Corrosion is the degradation of a metal caused by an electrochemical process. Large sums of money are spent each year repairing the effects of, or preventing, corrosion. Some metals, such as aluminum and copper, produce a protective layer when they corrode in air. The thin layer that forms on the surface of the metal prevents oxygen from coming into contact with more of the metal atoms and thus “protects” the remaining metal from further corrosion. Iron corrodes (forms rust) when exposed to water and oxygen. The rust that forms on iron metal flakes off, exposing fresh metal, which also corrodes. One way to prevent, or slow, corrosion is by coating the metal. Coating prevents water and oxygen from contacting the metal. Paint or other coatings will slow corrosion, but they are not effective once scratched. Zinc-plated or galvanized iron exploits the fact that zinc is more likely to oxidize than iron. As long as the coating remains, even if scratched, the zinc will oxidize before the iron. Another method for protecting metals is

cathodic protection. In this method, an easily oxidized and inexpensive metal, often zinc or magnesium (the sacrificial anode), is electrically connected to the metal that must be protected. The more active metal is the sacrificial anode, and is the anode in a galvanic cell. The “protected” metal is the cathode, and remains unoxidized. One advantage of cathodic protection is that the sacrificial anode can be monitored and replaced if needed.

Chemistry End of Chapter Exercises

Exercise:

Problem: Which member of each pair of metals is more likely to corrode (oxidize)?

(a) Mg or Ca

(b) Au or Hg

(c) Fe or Zn

(d) Ag or Pt

Exercise:

Problem:

Consider the following metals: Ag, Au, Mg, Ni, and Zn. Which of these metals could be used as a sacrificial anode in the cathodic protection of an underground steel storage tank? Steel is mostly iron, so use -0.447 V as the standard reduction potential for steel.

Solution:

Mg and Zn

Exercise:

Problem:

Aluminum ($E_{\text{Al}^{3+}/\text{Al}}^\circ = -2.07\text{ V}$) is more easily oxidized than iron ($E_{\text{Fe}^{3+}/\text{Fe}}^\circ = -0.477\text{ V}$), and yet when both are exposed to the environment, untreated aluminum has very good corrosion resistance while the corrosion resistance of untreated iron is poor. Explain this observation.

Exercise:

Problem:

If a sample of iron and a sample of zinc come into contact, the zinc corrodes but the iron does not. If a sample of iron comes into contact with a sample of copper, the iron corrodes but the copper does not. Explain this phenomenon.

Solution:

Both examples involve cathodic protection. The (sacrificial) anode is the metal that corrodes (oxidizes or reacts). In the case of iron (-0.447 V) and zinc (-0.7618 V), zinc has a more negative standard reduction potential and so serves as the anode. In the case of iron and copper (0.34 V), iron has the smaller standard reduction potential and so corrodes (serves as the anode).

Exercise:**Problem:**

Suppose you have three different metals, A, B, and C. When metals A and B come into contact, B corrodes and A does not corrode. When metals A and C come into contact, A corrodes and C does not corrode. Based on this information, which metal corrodes and which metal does not corrode when B and C come into contact?

Exercise:**Problem:**

Why would a sacrificial anode made of lithium metal be a bad choice despite its $E_{\text{Li}^+/\text{Li}} = -3.04\text{ V}$, which appears to be able to protect all the other metals listed in the standard reduction potential table?

Solution:

While the reduction potential of lithium would make it capable of protecting the other metals, this high potential is also indicative of how reactive lithium is; it would have a spontaneous reaction with most substances. This means that the lithium would react quickly with other substances, even those that would not oxidize the metal it is attempting to protect. Reactivity like this means the sacrificial anode would be depleted rapidly and need to be replaced frequently. (Optional additional reason: fire hazard in the presence of water.)

Glossary**cathodic protection**

method of protecting metal by using a sacrificial anode and effectively making the metal that needs protecting the cathode, thus preventing its oxidation

corrosion

degradation of metal through an electrochemical process

galvanized iron

method for protecting iron by covering it with zinc, which will oxidize before the iron;
zinc-plated iron

sacrificial anode

more active, inexpensive metal used as the anode in cathodic protection; frequently made from magnesium or zinc

Electrolysis

By the end of this section, you will be able to:

- Describe electrolytic cells and their relationship to galvanic cells
- Perform various calculations related to electrolysis

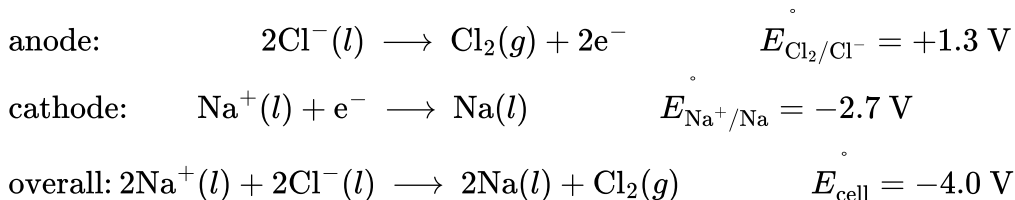
In galvanic cells, chemical energy is converted into electrical energy. The opposite is true for electrolytic cells. In **electrolytic cells**, electrical energy causes nonspontaneous reactions to occur in a process known as **electrolysis**. The charging electric car pictured in [\[link\]](#) at the beginning of this chapter shows one such process. Electrical energy is converted into the chemical energy in the battery as it is charged. Once charged, the battery can be used to power the automobile.

The same principles are involved in electrolytic cells as in galvanic cells. We will look at three electrolytic cells and the quantitative aspects of electrolysis.

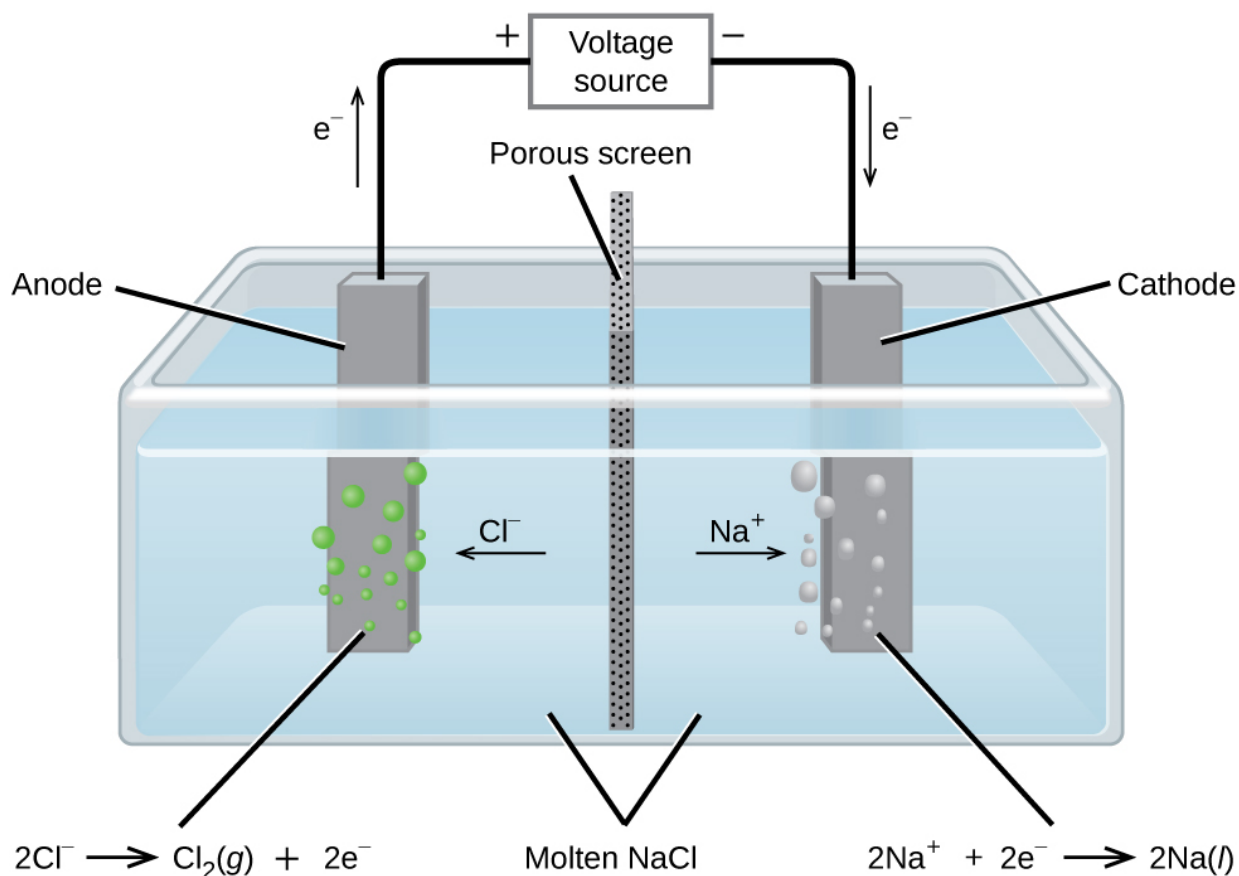
The Electrolysis of Molten Sodium Chloride

In molten sodium chloride, the ions are free to migrate to the electrodes of an electrolytic cell. A simplified diagram of the cell commercially used to produce sodium metal and chlorine gas is shown in [\[link\]](#). Sodium is a strong reducing agent and chlorine is used to purify water, and is used in antiseptics and in paper production. The reactions are

Equation:



The power supply (battery) must supply a minimum of 4 V, but, in practice, the applied voltages are typically higher because of inefficiencies in the process itself.

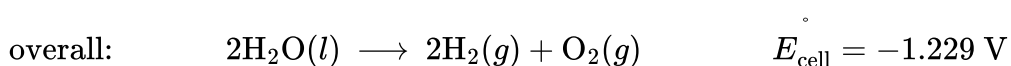
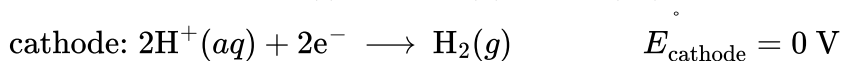


Passing an electric current through molten sodium chloride decomposes the material into sodium metal and chlorine gas. Care must be taken to keep the products separated to prevent the spontaneous formation of sodium chloride.

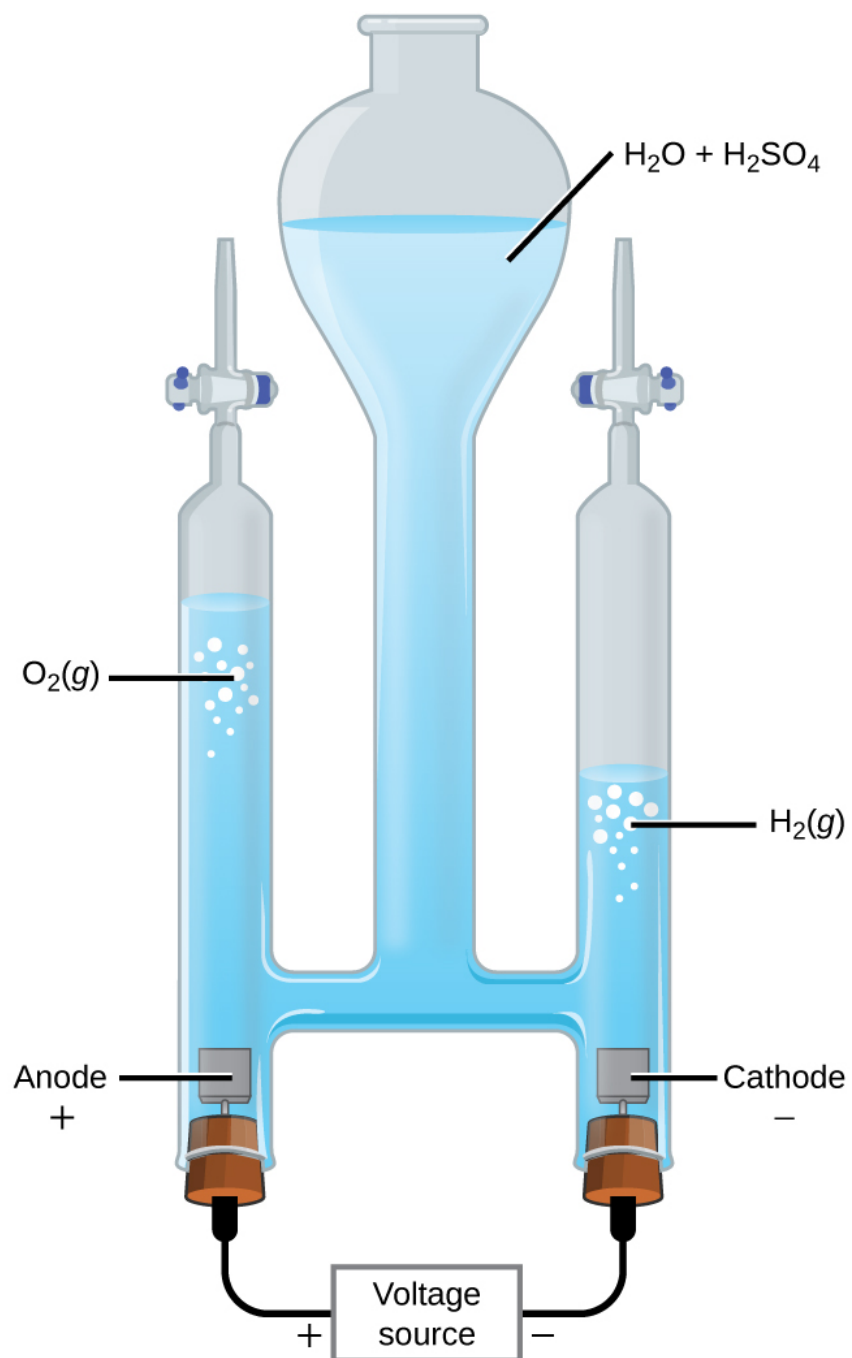
The Electrolysis of Water

It is possible to split water into hydrogen and oxygen gas by electrolysis. Acids are typically added to increase the concentration of hydrogen ion in solution ([link](#)). The reactions are

Equation:



Note that the sulfuric acid is not consumed and that the volume of hydrogen gas produced is twice the volume of oxygen gas produced. The minimum applied voltage is 1.229 V.

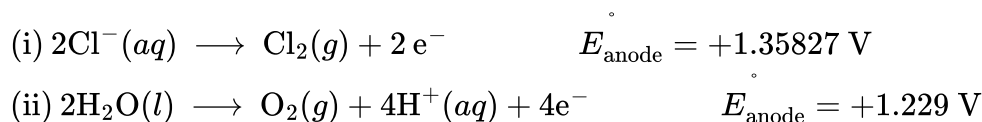


Water decomposes into oxygen and hydrogen gas during electrolysis. Sulfuric acid was added to increase the concentration of hydrogen ions and the total number of ions in solution, but does not take part in the reaction. The volume of hydrogen gas collected is twice the volume of oxygen gas collected, due to the stoichiometry of the reaction.

The Electrolysis of Aqueous Sodium Chloride

The electrolysis of aqueous sodium chloride is the more common example of electrolysis because more than one species can be oxidized and reduced. Considering the anode first, the possible reactions are

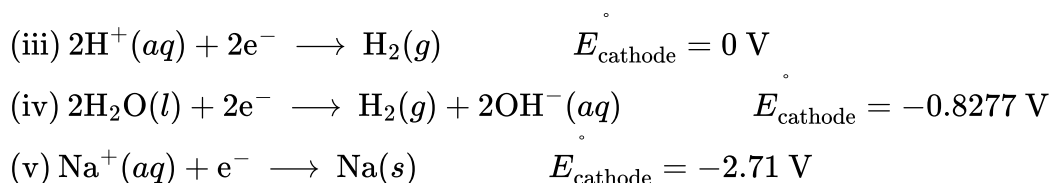
Equation:



These values suggest that water should be oxidized at the anode because a smaller potential would be needed—using reaction (ii) for the oxidation would give a less-negative cell potential. When the experiment is run, it turns out chlorine, not oxygen, is produced at the anode. The unexpected process is so common in electrochemistry that it has been given the name **overpotential**. The **overpotential** is the difference between the theoretical cell voltage and the actual voltage that is necessary to cause electrolysis. It turns out that the overpotential for oxygen is rather high and effectively makes the reduction potential more positive. As a result, under normal conditions, chlorine gas is what actually forms at the anode.

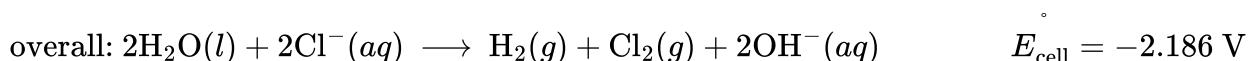
Now consider the cathode. Three reductions could occur:

Equation:



Reaction (v) is ruled out because it has such a negative reduction potential. Under standard state conditions, reaction (iii) would be preferred to reaction (iv). However, the pH of a sodium chloride solution is 7, so the concentration of hydrogen ions is only $1 \times 10^{-7} \text{ M}$. At such low concentrations, reaction (iii) is unlikely and reaction (iv) occurs. The overall reaction is then

Equation:

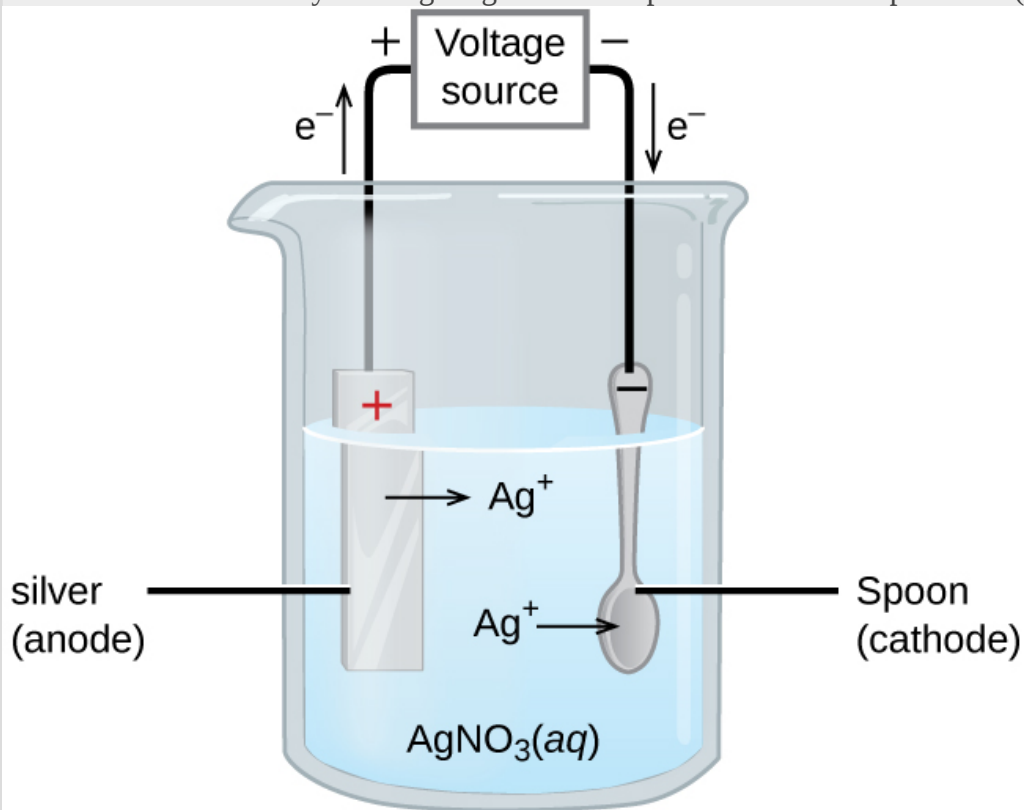


As the reaction proceeds, hydroxide ions replace chloride ions in solution. Thus, sodium hydroxide can be obtained by evaporating the water after the electrolysis is complete. Sodium hydroxide is valuable in its own right and is used for things like oven cleaner, drain opener, and in the production of paper, fabrics, and soap.

Note:

Electroplating

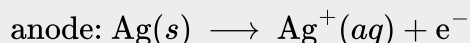
An important use for electrolytic cells is in **electroplating**. Electroplating results in a thin coating of one metal on top of a conducting surface. Reasons for electroplating include making the object more corrosion resistant, strengthening the surface, producing a more attractive finish, or for purifying metal. The metals commonly used in electroplating include cadmium, chromium, copper, gold, nickel, silver, and tin. Common consumer products include silver-plated or gold-plated tableware, chrome-plated automobile parts, and jewelry. We can get an idea of how this works by investigating how silver-plated tableware is produced ([link](#)).



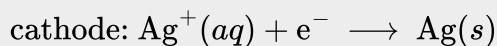
The spoon, which is made of an inexpensive metal, is connected to the negative terminal of the voltage source and acts as the cathode. The anode is a silver electrode. Both electrodes are immersed in a silver nitrate solution. When a steady current is passed through the solution, the net result is that silver metal is removed from the anode and deposited on the cathode.

In the figure, the anode consists of a silver electrode, shown on the left. The cathode is located on the right and is the spoon, which is made from inexpensive metal. Both electrodes are immersed in a solution of silver nitrate. As the potential is increased, current flows. Silver metal is lost at the anode as it goes into solution.

Equation:



The mass of the cathode increases as silver ions from the solution are deposited onto the spoon

Equation:

The net result is the transfer of silver metal from the anode to the cathode. The quality of the object is usually determined by the thickness of the deposited silver and the rate of deposition.

Quantitative Aspects of Electrolysis

The amount of current that is allowed to flow in an electrolytic cell is related to the number of moles of electrons. The number of moles of electrons can be related to the reactants and products using stoichiometry. Recall that the SI unit for current (I) is the ampere (A), which is the equivalent of 1 coulomb per second ($1 \text{ A} = 1 \frac{\text{C}}{\text{s}}$). The total charge (Q , in coulombs) is given by

Equation:

$$Q = I \times t = n \times F$$

Where t is the time in seconds, n the number of moles of electrons, and F is the Faraday constant.

Moles of electrons can be used in stoichiometry problems. The time required to deposit a specified amount of metal might also be requested, as in the second of the following examples.

Example:**Converting Current to Moles of Electrons**

In one process used for electroplating silver, a current of 10.23 A was passed through an electrolytic cell for exactly 1 hour. How many moles of electrons passed through the cell? What mass of silver was deposited at the cathode from the silver nitrate solution?

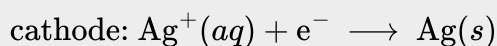
Solution

Faraday's constant can be used to convert the charge (Q) into moles of electrons (n). The charge is the current (I) multiplied by the time

Equation:

$$n = \frac{Q}{F} = \frac{\frac{10.23 \text{ C}}{\text{s}} \times 1 \text{ hr} \times \frac{60 \text{ min}}{\text{hr}} \times \frac{60 \text{ s}}{\text{min}}}{96,485 \text{ C/mol e}^-} = \frac{36,830 \text{ C}}{96,485 \text{ C/mol e}^-} = 0.3817 \text{ mol e}^-$$

From the problem, the solution contains AgNO_3 , so the reaction at the cathode involves 1 mole of electrons for each mole of silver

Equation:

The atomic mass of silver is 107.9 g/mol, so

Equation:

$$\text{mass Ag} = 0.3817 \text{ mol e}^- \times \frac{1 \text{ mol Ag}}{1 \text{ mol e}^-} \times \frac{107.9 \text{ g Ag}}{1 \text{ mol Ag}} = 41.19 \text{ g Ag}$$

Check your answer: From the stoichiometry, 1 mole of electrons would produce 1 mole of silver. Less than one-half a mole of electrons was involved and less than one-half a mole of silver was produced.

Check Your Learning

Aluminum metal can be made from aluminum ions by electrolysis. What is the half-reaction at the cathode? What mass of aluminum metal would be recovered if a current of $2.50 \times 10^3 \text{ A}$ passed through the solution for 15.0 minutes? Assume the yield is 100%.

Note:

Answer:



Example:

Time Required for Deposition

In one application, a 0.010-mm layer of chromium must be deposited on a part with a total surface area of 3.3 m^2 from a solution of containing chromium(III) ions. How long would it take to deposit the layer of chromium if the current was 33.46 A? The density of chromium (metal) is 7.19 g/cm^3 .

Solution

This problem brings in a number of topics covered earlier. An outline of what needs to be done is:

- If the total charge can be determined, the time required is just the charge divided by the current
- The total charge can be obtained from the amount of Cr needed and the stoichiometry
- The amount of Cr can be obtained using the density and the volume Cr required
- The volume Cr required is the thickness times the area

Solving in steps, and taking care with the units, the volume of Cr required is

Equation:

$$\text{volume} = \left(0.010 \text{ mm} \times \frac{1 \text{ cm}}{10 \text{ mm}} \right) \times \left(3.3 \text{ m}^2 \times \left(\frac{10,000 \text{ cm}^2}{1 \text{ m}^2} \right) \right) = 33 \text{ cm}^3$$

Cubic centimeters were used because they match the volume unit used for the density. The amount of Cr is then

Equation:

$$\text{mass} = \text{volume} \times \text{density} = 33 \text{ cm}^3 \times \frac{7.19 \text{ g}}{\text{cm}^3} = 237 \text{ g Cr}$$

Equation:

$$\text{mol Cr} = 237 \text{ g Cr} \times \frac{1 \text{ mol Cr}}{52.00 \text{ g Cr}} = 4.56 \text{ mol Cr}$$

Since the solution contains chromium(III) ions, 3 moles of electrons are required per mole of Cr. The total charge is then

Equation:

$$Q = 4.56 \text{ mol Cr} \times \frac{3 \text{ mol e}^-}{1 \text{ mol Cr}} \times \frac{96485 \text{ C}}{\text{mol e}^-} = 1.32 \times 10^6 \text{ C}$$

The time required is then

Equation:

$$t = \frac{Q}{I} = \frac{1.32 \times 10^6 \text{ C}}{33.46 \text{ C/s}} = 3.95 \times 10^4 \text{ s} = 11.0 \text{ hr}$$

Check your answer: In a long problem like this, a single check is probably not enough. Each of the steps gives a reasonable number, so things are probably correct. Pay careful attention to unit conversions and the stoichiometry.

Check Your Learning

What mass of zinc is required to galvanize the top of a $3.00 \text{ m} \times 5.50 \text{ m}$ sheet of iron to a thickness of 0.100 mm of zinc? If the zinc comes from a solution of $\text{Zn}(\text{NO}_3)_2$ and the current is 25.5 A , how long will it take to galvanize the top of the iron? The density of zinc is 7.140 g/cm^3 .

Note:

Answer:

11.8 kg Zn requires 382 hours.

Key Concepts and Summary

Using electricity to force a nonspontaneous process to occur is electrolysis. Electrolytic cells are electrochemical cells with negative cell potentials (meaning a positive Gibbs free energy), and so are nonspontaneous. Electrolysis can occur in electrolytic cells by introducing a power supply, which supplies the energy to force the electrons to flow in the nonspontaneous direction. Electrolysis is done in solutions, which contain enough ions so current can flow. If the solution contains only one material, like the electrolysis of molten sodium chloride, it is a simple matter

to determine what is oxidized and what is reduced. In more complicated systems, like the electrolysis of aqueous sodium chloride, more than one species can be oxidized or reduced and the standard reduction potentials are used to determine the most likely oxidation (the half-reaction with the largest [most positive] standard reduction potential) and reduction (the half-reaction with the smallest [least positive] standard reduction potential). Sometimes unexpected half-reactions occur because of overpotential. Overpotential is the difference between the theoretical half-reaction reduction potential and the actual voltage required. When present, the applied potential must be increased, making it possible for a different reaction to occur in the electrolytic cell. The total charge, Q , that passes through an electrolytic cell can be expressed as the current (I) multiplied by time ($Q = It$) or as the moles of electrons (n) multiplied by Faraday's constant ($Q = nF$). These relationships can be used to determine things like the amount of material used or generated during electrolysis, how long the reaction must proceed, or what value of the current is required.

Key Equations

- $Q = I \times t = n \times F$

Chemistry End of Chapter Exercises

Exercise:

Problem:

Identify the reaction at the anode, reaction at the cathode, the overall reaction, and the approximate potential required for the electrolysis of the following molten salts. Assume standard states and that the standard reduction potentials in [Appendix L](#) are the same as those at each of the melting points. Assume the efficiency is 100%.

- (a) CaCl_2
- (b) LiH
- (c) AlCl_3
- (d) CrBr_3

Exercise:

Problem:

What mass of each product is produced in each of the electrolytic cells of the previous problem if a total charge of $3.33 \times 10^5 \text{ C}$ passes through each cell? Assume the voltage is sufficient to perform the reduction.

Solution:

(a) mass Ca = 69.1 g; (b) mass Li = 23.9 g; (c) mass Al = 31.0 g; (d) mass Cl₂ = 122 g; mass H₂ = 3.48 g; (e) mass Cr = 59.8 g; mass Br₂ = 276 g

Exercise:

Problem:

How long would it take to reduce 1 mole of each of the following ions using the current indicated? Assume the voltage is sufficient to perform the reduction.

(a) Al³⁺, 1.234 A

(b) Ca²⁺, 22.2 A

(c) Cr⁵⁺, 37.45 A

(d) Au³⁺, 3.57 A

Exercise:

Problem:

A current of 2.345 A passes through the cell shown in [\[link\]](#) for 45 minutes. What is the volume of the hydrogen collected at room temperature if the pressure is exactly 1 atm? Assume the voltage is sufficient to perform the reduction. (Hint: Is hydrogen the only gas present above the water?)

Solution:

0.79 L

Exercise:

Problem:

An irregularly shaped metal part made from a particular alloy was galvanized with zinc using a Zn(NO₃)₂ solution. When a current of 2.599 A was used, it took exactly 1 hour to deposit a 0.01123-mm layer of zinc on the part. What was the total surface area of the part? The density of zinc is 7.140 g/cm³. Assume the efficiency is 100%.

Glossary

electrolysis

process using electrical energy to cause a nonspontaneous process to occur

electrolytic cell

electrochemical cell in which electrolysis is used; electrochemical cell with negative cell potentials

electroplating

depositing a thin layer of one metal on top of a conducting surface

overpotential

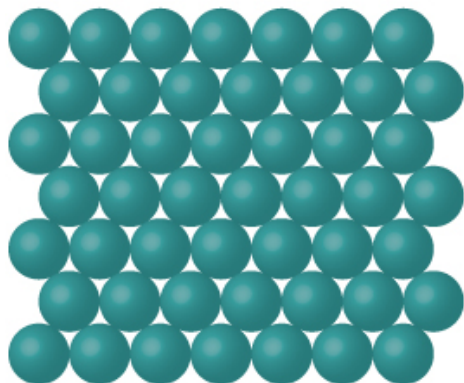
difference between the theoretical potential and actual potential in an electrolytic cell; the “extra” voltage required to make some nonspontaneous electrochemical reaction to occur

The Solid State of Matter

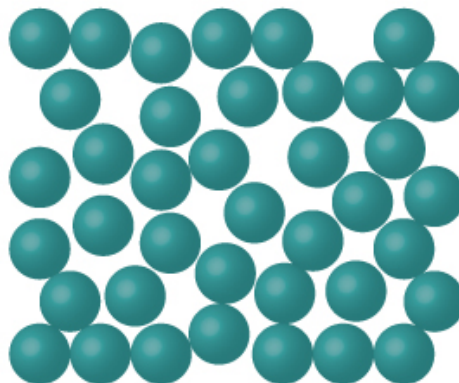
By the end of this section, you will be able to:

- Define and describe the bonding and properties of ionic, molecular, metallic, and covalent network crystalline solids
- Describe the main types of crystalline solids: ionic solids, metallic solids, covalent network solids, and molecular solids
- Explain the ways in which crystal defects can occur in a solid

When most liquids are cooled, they eventually freeze and form **crystalline solids**, solids in which the atoms, ions, or molecules are arranged in a definite repeating pattern. It is also possible for a liquid to freeze before its molecules become arranged in an orderly pattern. The resulting materials are called **amorphous solids** or noncrystalline solids (or, sometimes, glasses). The particles of such solids lack an ordered internal structure and are randomly arranged ([link](#)).



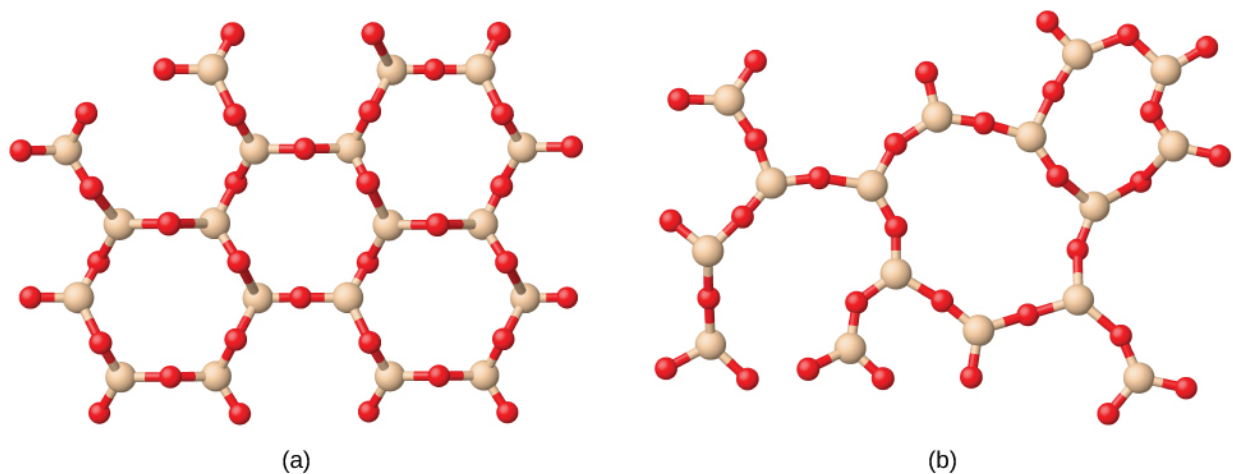
Crystalline



Amorphous

The entities of a solid phase may be arranged in a regular, repeating pattern (crystalline solids) or randomly (amorphous).

Metals and ionic compounds typically form ordered, crystalline solids. Substances that consist of large molecules, or a mixture of molecules whose movements are more restricted, often form amorphous solids. For examples, candle waxes are amorphous solids composed of large hydrocarbon molecules. Some substances, such as silicon dioxide (shown in [link](#)), can form either crystalline or amorphous solids, depending on the conditions under which it is produced. Also, amorphous solids may undergo a transition to the crystalline state under appropriate conditions.

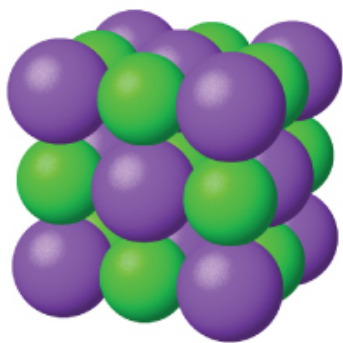


(a) Silicon dioxide, SiO_2 , is abundant in nature as one of several crystalline forms of the mineral quartz. (b) Rapid cooling of molten SiO_2 yields an amorphous solid known as “fused silica”.

Crystalline solids are generally classified according to the nature of the forces that hold its particles together. These forces are primarily responsible for the physical properties exhibited by the bulk solids. The following sections provide descriptions of the major types of crystalline solids: ionic, metallic, covalent network, and molecular.

Ionic Solids

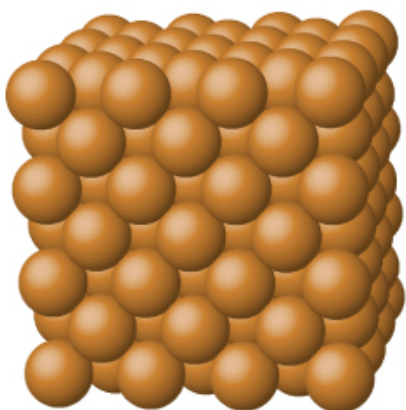
Ionic solids, such as sodium chloride and nickel oxide, are composed of positive and negative ions that are held together by electrostatic attractions, which can be quite strong ([link](#)). Many ionic crystals also have high melting points. This is due to the very strong attractions between the ions—in ionic compounds, the attractions between full charges are (much) larger than those between the partial charges in polar molecular compounds. This will be looked at in more detail in a later discussion of lattice energies. Although they are hard, they also tend to be brittle, and they shatter rather than bend. Ionic solids do not conduct electricity; however, they do conduct when molten or dissolved because their ions are free to move. Many simple compounds formed by the reaction of a metallic element with a nonmetallic element are ionic.



Sodium chloride is an ionic solid.

Metallic Solids

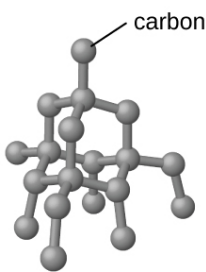
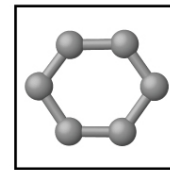
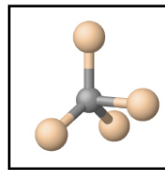
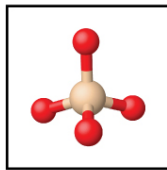
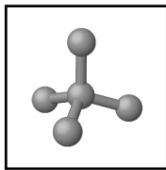
Metallic solids such as crystals of copper, aluminum, and iron are formed by metal atoms [\[link\]](#). The structure of metallic crystals is often described as a uniform distribution of atomic nuclei within a “sea” of delocalized electrons. The atoms within such a metallic solid are held together by a unique force known as *metallic bonding* that gives rise to many useful and varied bulk properties. All exhibit high thermal and electrical conductivity, metallic luster, and malleability. Many are very hard and quite strong. Because of their malleability (the ability to deform under pressure or hammering), they do not shatter and, therefore, make useful construction materials. The melting points of the metals vary widely. Mercury is a liquid at room temperature, and the alkali metals melt below 200 °C. Several post-transition metals also have low melting points, whereas the transition metals melt at temperatures above 1000 °C. These differences reflect differences in strengths of metallic bonding among the metals.



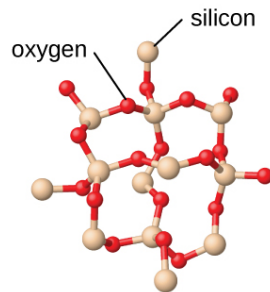
Copper is a metallic solid.

Covalent Network Solid

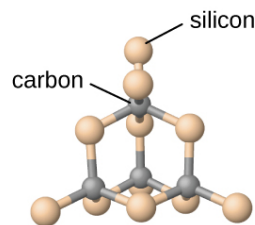
Covalent network solids include crystals of diamond, silicon, some other nonmetals, and some covalent compounds such as silicon dioxide (sand) and silicon carbide (carborundum, the abrasive on sandpaper). Many minerals have networks of covalent bonds. The atoms in these solids are held together by a network of covalent bonds, as shown in [\[link\]](#). To break or to melt a covalent network solid, covalent bonds must be broken. Because covalent bonds are relatively strong, covalent network solids are typically characterized by hardness, strength, and high melting points. For example, diamond is one of the hardest substances known and melts above 3500 °C.



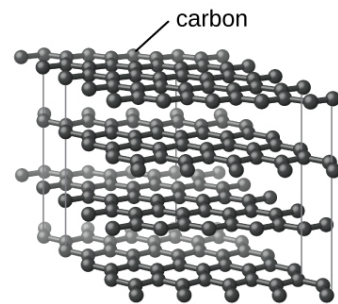
diamond



silicon dioxide



silicon carbide

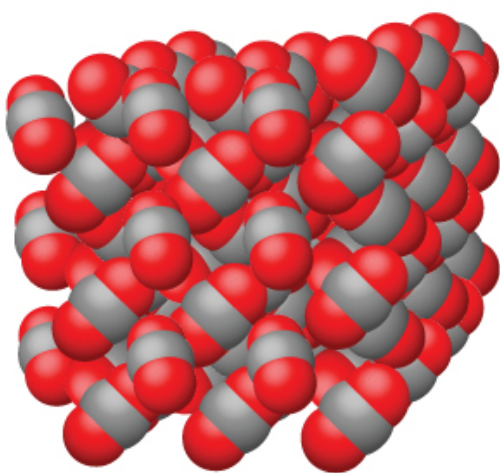


graphite

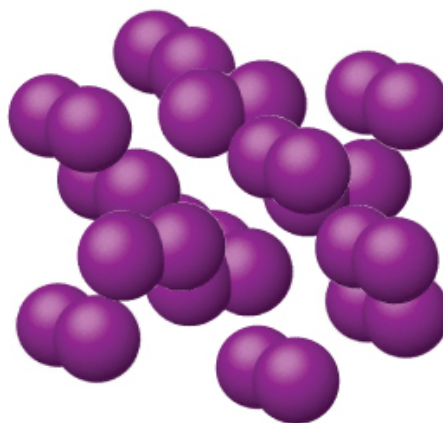
A covalent crystal contains a three-dimensional network of covalent bonds, as illustrated by the structures of diamond, silicon dioxide, silicon carbide, and graphite. Graphite is an exceptional example, composed of planar sheets of covalent crystals that are held together in layers by noncovalent forces. Unlike typical covalent solids, graphite is very soft and electrically conductive.

Molecular Solid

Molecular solids, such as ice, sucrose (table sugar), and iodine, as shown in [\[link\]](#), are composed of neutral molecules. The strengths of the attractive forces between the units present in different crystals vary widely, as indicated by the melting points of the crystals. Small symmetrical molecules (nonpolar molecules), such as H_2 , N_2 , O_2 , and F_2 , have weak attractive forces and form molecular solids with very low melting points (below $-200\text{ }^\circ\text{C}$). Substances consisting of larger, nonpolar molecules have larger attractive forces and melt at higher temperatures. Molecular solids composed of molecules with permanent dipole moments (polar molecules) melt at still higher temperatures. Examples include ice (melting point, $0\text{ }^\circ\text{C}$) and table sugar (melting point, $185\text{ }^\circ\text{C}$).



carbon dioxide



iodine

Carbon dioxide (CO_2) consists of small, nonpolar molecules and forms a molecular solid with a melting point of $-78\text{ }^\circ\text{C}$. Iodine (I_2) consists of larger, nonpolar molecules and forms a molecular solid that melts at $114\text{ }^\circ\text{C}$.

Properties of Solids

A crystalline solid, like those listed in [\[link\]](#), has a precise melting temperature because each atom or molecule of the same type is held in place with the same forces or energy. Thus, the attractions between the units that make up the crystal all have the same strength and all require the same amount of energy to be broken. The gradual softening of an amorphous material differs dramatically from the distinct melting of a crystalline solid. This results from the structural nonequivalence of the molecules in the amorphous

solid. Some forces are weaker than others, and when an amorphous material is heated, the weakest intermolecular attractions break first. As the temperature is increased further, the stronger attractions are broken. Thus amorphous materials soften over a range of temperatures.

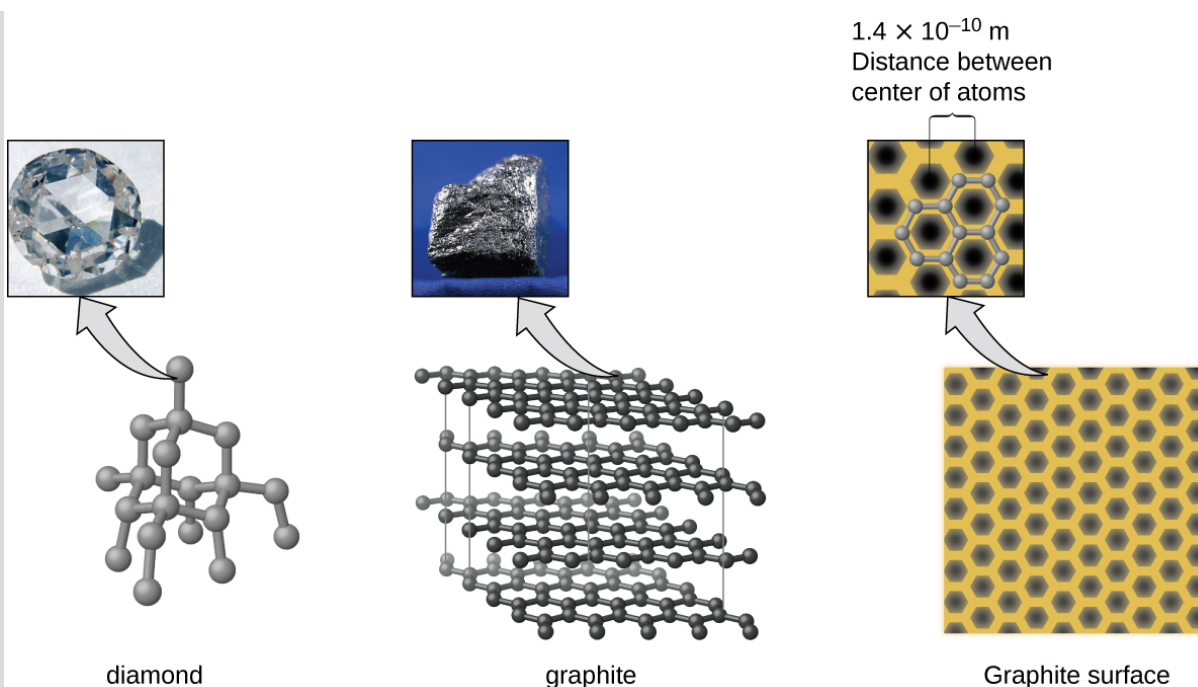
Types of Crystalline Solids and Their Properties				
Type of Solid	Type of Particles	Type of Attractions	Properties	Examples
ionic	ions	ionic bonds	hard, brittle, conducts electricity as a liquid but not as a solid, high to very high melting points	NaCl, Al ₂ O ₃
metallic	atoms of electropositive elements	metallic bonds	shiny, malleable, ductile, conducts heat and electricity well, variable hardness and melting temperature	Cu, Fe, Ti, Pb, U
covalent network	atoms of electronegative elements	covalent bonds	very hard, not conductive, very high melting points	C (diamond), SiO ₂ , SiC

Types of Crystalline Solids and Their Properties				
Type of Solid	Type of Particles	Type of Attractions	Properties	Examples
molecular	molecules (or atoms)	IMFs	variable hardness, variable brittleness, not conductive, low melting points	H ₂ O, CO ₂ , I ₂ , C ₁₂ H ₂₂ O ₁₁

Note:

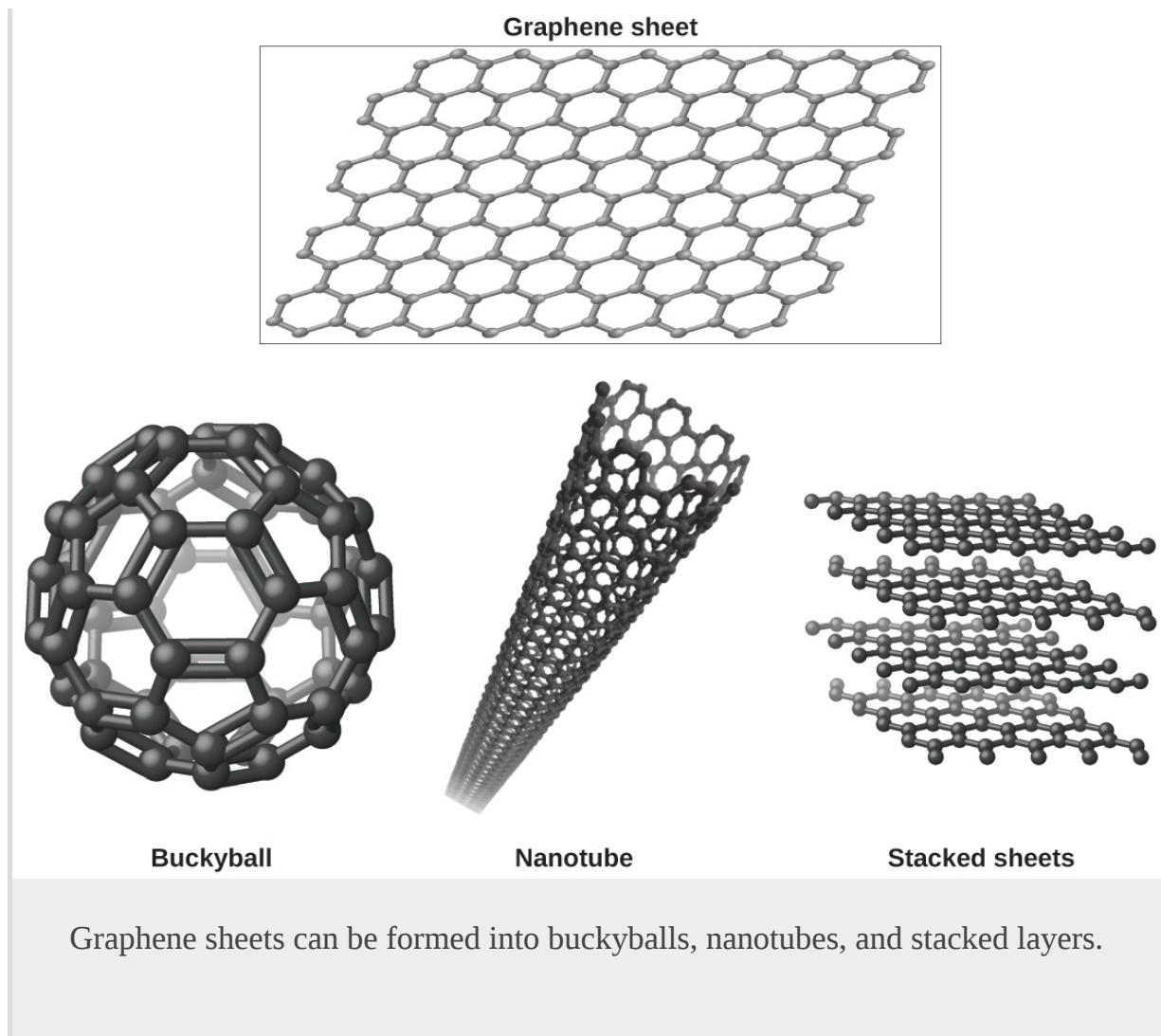
Graphene: Material of the Future

Carbon is an essential element in our world. The unique properties of carbon atoms allow the existence of carbon-based life forms such as ourselves. Carbon forms a huge variety of substances that we use on a daily basis, including those shown in [\[link\]](#). You may be familiar with diamond and graphite, the two most common *allotropes* of carbon. (Allotropes are different structural forms of the same element.) Diamond is one of the hardest-known substances, whereas graphite is soft enough to be used as pencil lead. These very different properties stem from the different arrangements of the carbon atoms in the different allotropes.



Diamond is extremely hard because of the strong bonding between carbon atoms in all directions. Graphite (in pencil lead) rubs off onto paper due to the weak attractions between the carbon layers. An image of a graphite surface shows the distance between the centers of adjacent carbon atoms. (credit left photo: modification of work by Steve Jurvetson; credit middle photo: modification of work by United States Geological Survey)

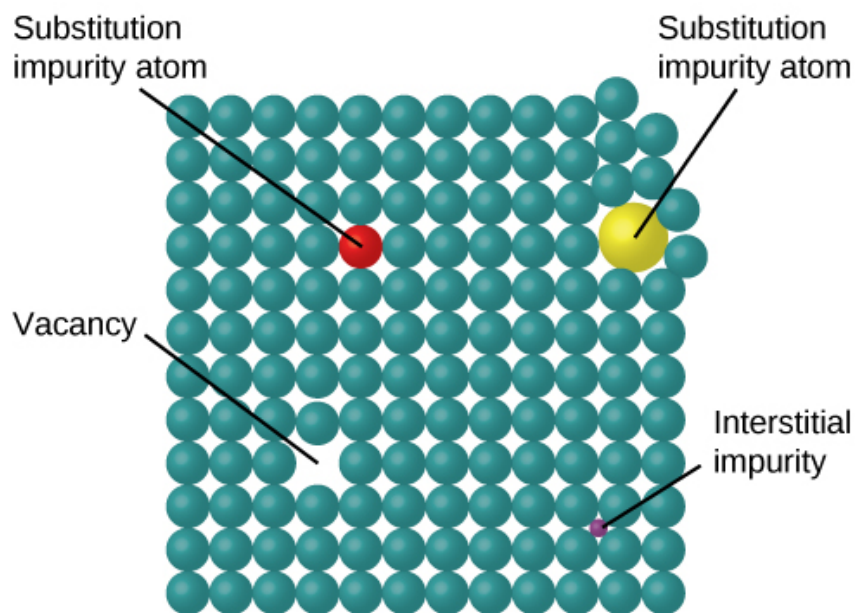
You may be less familiar with a recently discovered form of carbon: graphene. Graphene was first isolated in 2004 by using tape to peel off thinner and thinner layers from graphite. It is essentially a single sheet (one atom thick) of graphite. Graphene, illustrated in [\[link\]](#), is not only strong and lightweight, but it is also an excellent conductor of electricity and heat. These properties may prove very useful in a wide range of applications, such as vastly improved computer chips and circuits, better batteries and solar cells, and stronger and lighter structural materials. The 2010 Nobel Prize in Physics was awarded to Andre Geim and Konstantin Novoselov for their pioneering work with graphene.



Crystal Defects

In a crystalline solid, the atoms, ions, or molecules are arranged in a definite repeating pattern, but occasional defects may occur in the pattern. Several types of defects are known, as illustrated in [\[link\]](#). **Vacancies** are defects that occur when positions that should contain atoms or ions are vacant. Less commonly, some atoms or ions in a crystal may occupy positions, called **interstitial sites**, located between the regular positions for atoms. Other distortions are found in impure crystals, as, for example, when the cations, anions, or molecules of the impurity are too large to fit into the regular positions without distorting the structure. Trace amounts of impurities are sometimes added to a crystal (a process known as *doping*) in order to create defects in the structure that yield desirable changes in its properties. For example, silicon crystals

are doped with varying amounts of different elements to yield suitable electrical properties for their use in the manufacture of semiconductors and computer chips.



Types of crystal defects include vacancies, interstitial atoms, and substitutions impurities.

Key Concepts and Summary

Some substances form crystalline solids consisting of particles in a very organized structure; others form amorphous (noncrystalline) solids with an internal structure that is not ordered. The main types of crystalline solids are ionic solids, metallic solids, covalent network solids, and molecular solids. The properties of the different kinds of crystalline solids are due to the types of particles of which they consist, the arrangements of the particles, and the strengths of the attractions between them. Because their particles experience identical attractions, crystalline solids have distinct melting temperatures; the particles in amorphous solids experience a range of interactions, so they soften gradually and melt over a range of temperatures. Some crystalline solids have defects in the definite repeating pattern of their particles. These defects (which include vacancies, atoms or ions not in the regular positions, and impurities) change physical properties such as electrical conductivity, which is exploited in the silicon crystals used to manufacture computer chips.

Chemistry End of Chapter Exercises

Exercise:

Problem: What types of liquids typically form amorphous solids?

Exercise:

Problem:

At very low temperatures oxygen, O_2 , freezes and forms a crystalline solid. Which best describes these crystals?

- (a) ionic
 - (b) covalent network
 - (c) metallic
 - (d) amorphous
 - (e) molecular crystals
-

Solution:

- (e) molecular crystals

Exercise:

Problem:

As it cools, olive oil slowly solidifies and forms a solid over a range of temperatures. Which best describes the solid?

- (a) ionic
- (b) covalent network
- (c) metallic
- (d) amorphous
- (e) molecular crystals

Exercise:

Problem:

Explain why ice, which is a crystalline solid, has a melting temperature of $0\text{ }^{\circ}\text{C}$, whereas butter, which is an amorphous solid, softens over a range of temperatures.

Solution:

Ice has a crystalline structure stabilized by hydrogen bonding. These intermolecular forces are of comparable strength and thus require the same amount of energy to overcome. As a result, ice melts at a single temperature and not over a range of temperatures. The various, very large molecules that compose butter experience varied van der Waals attractions of various strengths that are overcome at various temperatures, and so the melting process occurs over a wide temperature range.

Exercise:**Problem:**

Identify the type of crystalline solid (metallic, network covalent, ionic, or molecular) formed by each of the following substances:

- (a) SiO_2
- (b) KCl
- (c) Cu
- (d) CO_2
- (e) C (diamond)
- (f) BaSO_4
- (g) NH_3
- (h) NH_4F
- (i) $\text{C}_2\text{H}_5\text{OH}$

Exercise:**Problem:**

Identify the type of crystalline solid (metallic, network covalent, ionic, or molecular) formed by each of the following substances:

- (a) CaCl_2
- (b) SiC
- (c) N_2
- (d) Fe
- (e) C (graphite)
- (f) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
- (g) HCl
- (h) NH_4NO_3
- (i) K_3PO_4

Solution:

(a) ionic; (b) covalent network; (c) molecular; (d) metallic; (e) covalent network;
 (f) molecular; (g) molecular; (h) ionic; (i) ionic

Exercise:

Problem:

Classify each substance in the table as either a metallic, ionic, molecular, or covalent network solid:

Substance	Appearance	Melting Point	Electrical Conductivity	Solubility in Water
X	lustrous, malleable	1500 °C	high	insoluble
Y	soft, yellow	113 °C	none	insoluble
Z	hard, white	800 °C	only if melted/dissolved	soluble

Exercise:**Problem:**

Classify each substance in the table as either a metallic, ionic, molecular, or covalent network solid:

Substance	Appearance	Melting Point	Electrical Conductivity	Solubility in Water
X	brittle, white	800 °C	only if melted/dissolved	soluble
Y	shiny, malleable	1100 °C	high	insoluble
Z	hard, colorless	3550 °C	none	insoluble

Solution:

X = ionic; Y = metallic; Z = covalent network

Exercise:**Problem:**

Identify the following substances as ionic, metallic, covalent network, or molecular solids:

Substance A is malleable, ductile, conducts electricity well, and has a melting point of 1135 °C. Substance B is brittle, does not conduct electricity as a solid but does when molten, and has a melting point of 2072 °C. Substance C is very hard, does not conduct electricity, and has a melting point of 3440 °C. Substance D is soft, does not conduct electricity, and has a melting point of 185 °C.

Exercise:

Problem:

Substance A is shiny, conducts electricity well, and melts at 975 °C. Substance A is likely a(n):

- (a) ionic solid
 - (b) metallic solid
 - (c) molecular solid
 - (d) covalent network solid
-

Solution:

- (b) metallic solid

Exercise:**Problem:**

Substance B is hard, does not conduct electricity, and melts at 1200 °C. Substance B is likely a(n):

- (a) ionic solid
- (b) metallic solid
- (c) molecular solid
- (d) covalent network solid

Glossary

amorphous solid

(also, noncrystalline solid) solid in which the particles lack an ordered internal structure

covalent network solid

solid whose particles are held together by covalent bonds

crystalline solid

solid in which the particles are arranged in a definite repeating pattern

interstitial sites

spaces between the regular particle positions in any array of atoms or ions

ionic solid

solid composed of positive and negative ions held together by strong electrostatic attractions

metallic solid

solid composed of metal atoms

molecular solid

solid composed of neutral molecules held together by intermolecular forces of attraction

vacancy

defect that occurs when a position that should contain an atom or ion is vacant

Lattice Structures in Crystalline Solids

By the end of this section, you will be able to:

- Describe the arrangement of atoms and ions in crystalline structures
- Compute ionic radii using unit cell dimensions
- Explain the use of X-ray diffraction measurements in determining crystalline structures

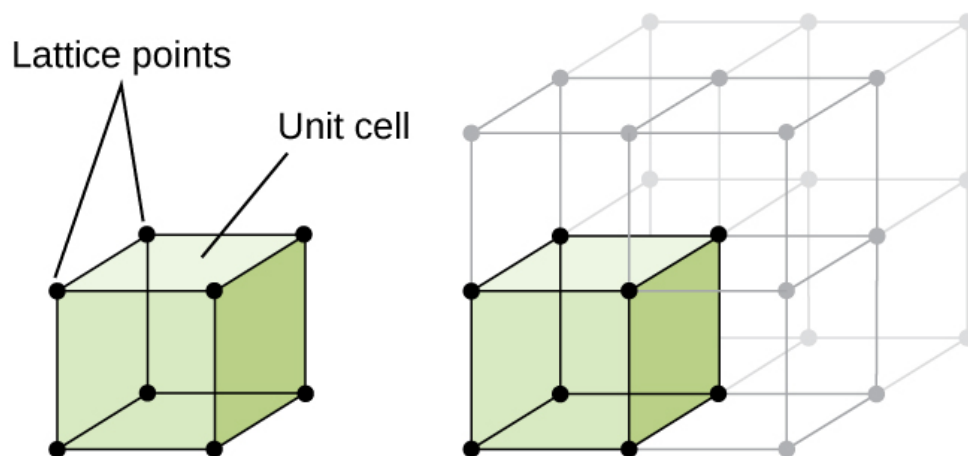
Over 90% of naturally occurring and man-made solids are crystalline. Most solids form with a regular arrangement of their particles because the overall attractive interactions between particles are maximized, and the total intermolecular energy is minimized, when the particles pack in the most efficient manner. The regular arrangement at an atomic level is often reflected at a macroscopic level. In this module, we will explore some of the details about the structures of metallic and ionic crystalline solids, and learn how these structures are determined experimentally.

The Structures of Metals

We will begin our discussion of crystalline solids by considering elemental metals, which are relatively simple because each contains only one type of atom. A pure metal is a crystalline solid with metal atoms packed closely together in a repeating pattern. Some of the properties of metals in general, such as their malleability and ductility, are largely due to having identical atoms arranged in a regular pattern. The different properties of one metal compared to another partially depend on the sizes of their atoms and the specifics of their spatial arrangements. We will explore the similarities and differences of four of the most common metal crystal geometries in the sections that follow.

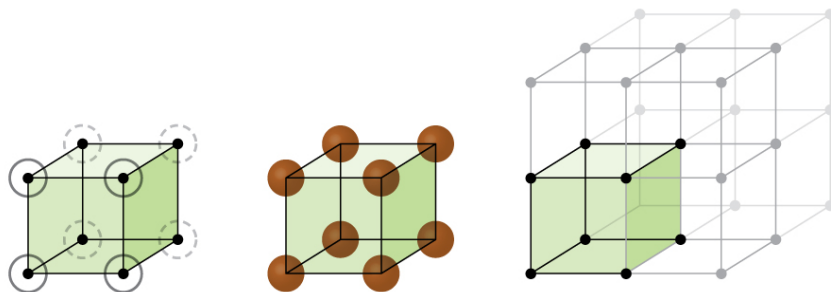
Unit Cells of Metals

The structure of a crystalline solid, whether a metal or not, is best described by considering its simplest repeating unit, which is referred to as its **unit cell**. The unit cell consists of lattice points that represent the locations of atoms or ions. The entire structure then consists of this unit cell repeating in three dimensions, as illustrated in [\[link\]](#).



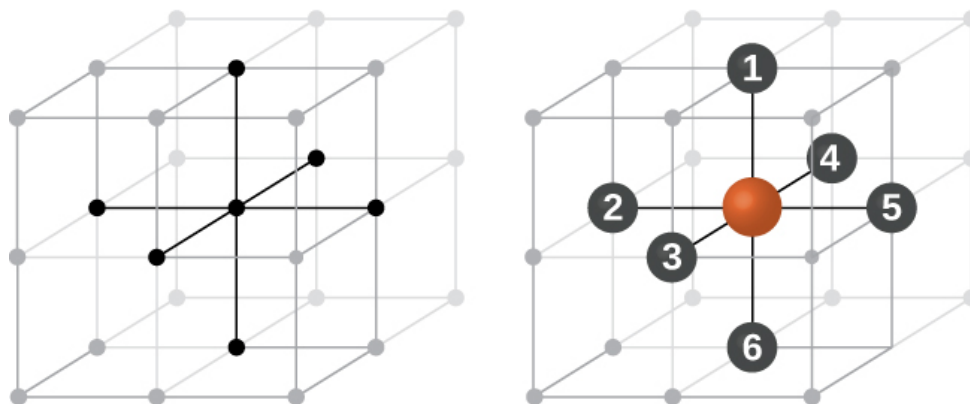
A unit cell shows the locations of lattice points repeating in all directions.

Let us begin our investigation of crystal lattice structure and unit cells with the most straightforward structure and the most basic unit cell. To visualize this, imagine taking a large number of identical spheres, such as tennis balls, and arranging them uniformly in a container. The simplest way to do this would be to make layers in which the spheres in one layer are directly above those in the layer below, as illustrated in [\[link\]](#). This arrangement is called **simple cubic structure**, and the unit cell is called the **simple cubic unit cell** or primitive cubic unit cell.



When metal atoms are arranged with spheres in one layer directly above or below spheres in another layer, the lattice structure is called simple cubic. Note that the spheres are in contact.

In a simple cubic structure, the spheres are not packed as closely as they could be, and they only “fill” about 52% of the volume of the container. This is a relatively inefficient arrangement, and only one metal (polonium, Po) crystallizes in a simple cubic structure. As shown in [\[link\]](#), a solid with this type of arrangement consists of planes (or layers) in which each atom contacts only the four nearest neighbors in its layer; one atom directly above it in the layer above; and one atom directly below it in the layer below. The number of other particles that each particle in a crystalline solid contacts is known as its **coordination number**. For a polonium atom in a simple cubic array, the coordination number is, therefore, six.

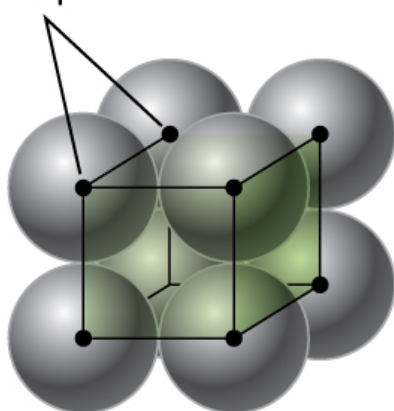


An atom in a simple cubic lattice structure contacts six other atoms, so it

has a coordination number of six.

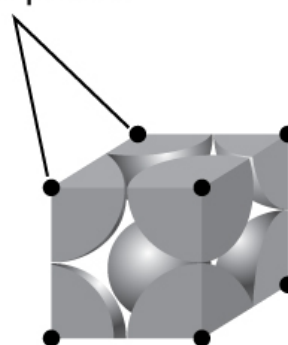
In a simple cubic lattice, the unit cell that repeats in all directions is a cube defined by the centers of eight atoms, as shown in [\[link\]](#). Atoms at adjacent corners of this unit cell contact each other, so the edge length of this cell is equal to two atomic radii, or one atomic diameter. A cubic unit cell contains only the parts of these atoms that are within it. Since an atom at a corner of a simple cubic unit cell is contained by a total of eight unit cells, only one-eighth of that atom is within a specific unit cell. And since each simple cubic unit cell has one atom at each of its eight “corners,” there is $8 \times \frac{1}{8} = 1$ atom within one simple cubic unit cell.

Lattice points



Simple cubic lattice cell

Lattice points



8 corners

A simple cubic lattice unit cell contains one-eighth of an atom at each of its eight corners, so it contains one atom total.

Example:

Calculation of Atomic Radius and Density for Metals, Part 1

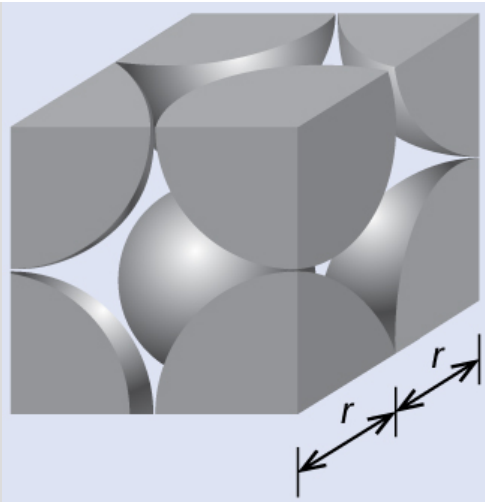
The edge length of the unit cell of alpha polonium is 336 pm.

(a) Determine the radius of a polonium atom.

(b) Determine the density of alpha polonium.

Solution

Alpha polonium crystallizes in a simple cubic unit cell:



(a) Two adjacent Po atoms contact each other, so the edge length of this cell is equal to two Po atomic radii: $l = 2r$. Therefore, the radius of Po is $r = \frac{l}{2} = \frac{336 \text{ pm}}{2} = 168 \text{ pm}$.

(b) Density is given by $\text{density} = \frac{\text{mass}}{\text{volume}}$. The density of polonium can be found by determining the density of its unit cell (the mass contained within a unit cell divided by the volume of the unit cell). Since a Po unit cell contains one-eighth of a Po atom at each of its eight corners, a unit cell contains one Po atom.

The mass of a Po unit cell can be found by:

Equation:

$$1 \text{ Po unit cell} \times \frac{1 \text{ Po atom}}{1 \text{ Po unit cell}} \times \frac{1 \text{ mol Po}}{6.022 \times 10^{23} \text{ Po atoms}} \times \frac{208.998 \text{ g}}{1 \text{ mol Po}} = 3.47 \times 10^{-22} \text{ g}$$

The volume of a Po unit cell can be found by:

Equation:

$$V = l^3 = (336 \times 10^{-10} \text{ cm})^3 = 3.79 \times 10^{-23} \text{ cm}^3$$

(Note that the edge length was converted from pm to cm to get the usual volume units for density.)

Therefore, the density of Po = $\frac{3.471 \times 10^{-22} \text{ g}}{3.79 \times 10^{-23} \text{ cm}^3} = 9.16 \text{ g/cm}^3$

Check Your Learning

The edge length of the unit cell for nickel is 0.3524 nm. The density of Ni is 8.90 g/cm^3 . Does nickel crystallize in a simple cubic structure? Explain.

Note:

Answer:

No. If Ni was simple cubic, its density would be given by:

$$1 \text{ Ni atom} \times \frac{1 \text{ mol Ni}}{6.022 \times 10^{23} \text{ Ni atoms}} \times \frac{58.693 \text{ g}}{1 \text{ mol Ni}} = 9.746 \times 10^{-23} \text{ g}$$

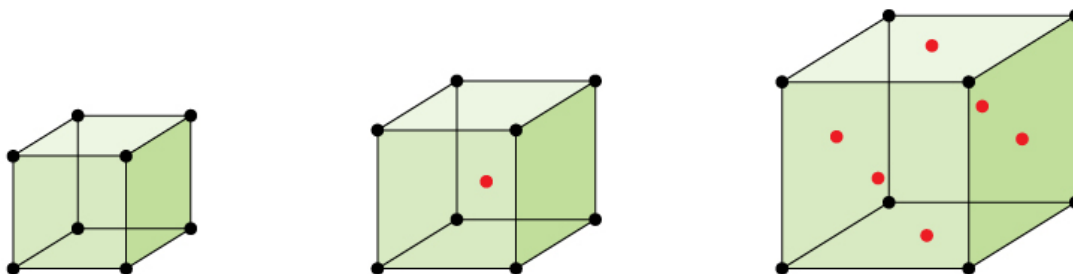
$$V = l^3 = (3.524 \times 10^{-8} \text{ cm})^3 = 4.376 \times 10^{-23} \text{ cm}^3$$

$$\text{Then the density of Ni would be} = \frac{9.746 \times 10^{-23} \text{ g}}{4.376 \times 10^{-23} \text{ cm}^3} = 2.23 \text{ g/cm}^3$$

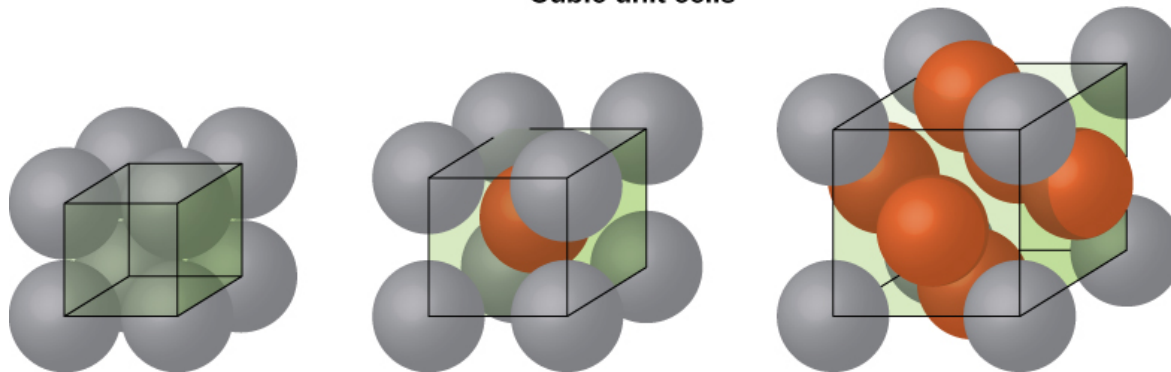
Since the actual density of Ni is not close to this, Ni does not form a simple cubic structure.

Most metal crystals are one of the four major types of unit cells. For now, we will focus on the three cubic unit cells: simple cubic (which we have already seen), **body-centered cubic unit cell**, and **face-centered cubic unit cell**—all of which are illustrated in [\[link\]](#). (Note that there are actually seven different lattice systems, some of which have more than one type of lattice, for a total of 14 different types of unit cells. We leave the more complicated geometries for later in this module.)

Lattice point locations



Cubic unit cells



Simple cubic

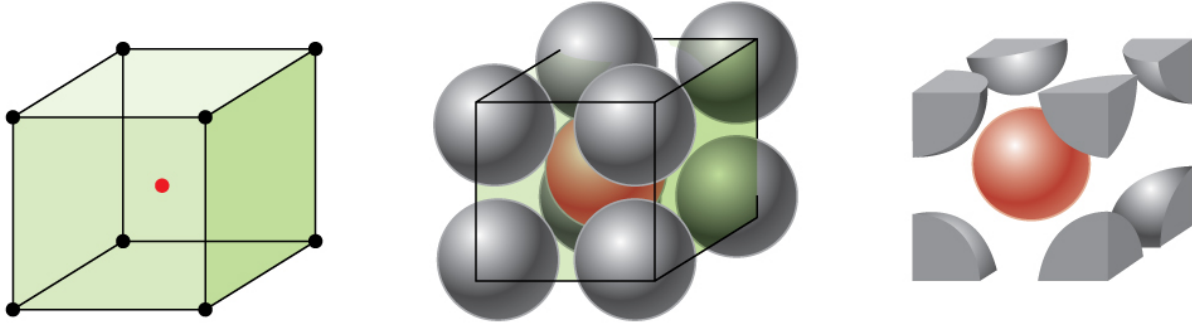
Body-centered cubic

Face-centered cubic

Cubic unit cells of metals show (in the upper figures) the locations of lattice points and (in the lower figures) metal atoms located in the unit cell.

Some metals crystallize in an arrangement that has a cubic unit cell with atoms at all of the corners and an atom in the center, as shown in [\[link\]](#). This is called a **body-centered cubic (BCC) solid**. Atoms in the corners of a BCC unit cell do not contact each other but contact the atom in the center. A BCC unit cell contains two atoms: one-eighth of an atom at each of the eight corners ($8 \times \frac{1}{8} = 1$ atom from the corners) plus one atom from the center. Any atom in this structure touches four atoms

in the layer above it and four atoms in the layer below it. Thus, an atom in a BCC structure has a coordination number of eight.

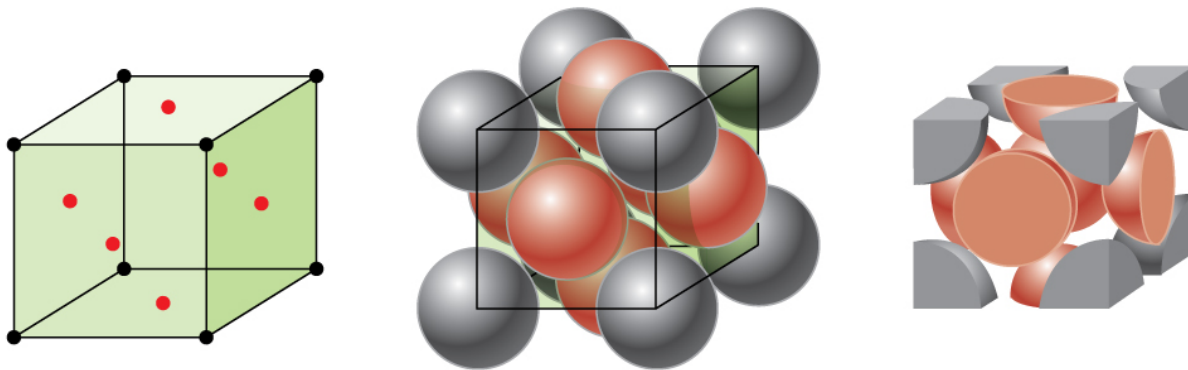


Body-centered cubic structure

In a body-centered cubic structure, atoms in a specific layer do not touch each other. Each atom touches four atoms in the layer above it and four atoms in the layer below it.

Atoms in BCC arrangements are much more efficiently packed than in a simple cubic structure, occupying about 68% of the total volume. Isomorphous metals with a BCC structure include K, Ba, Cr, Mo, W, and Fe at room temperature. (Elements or compounds that crystallize with the same structure are said to be **isomorphous**.)

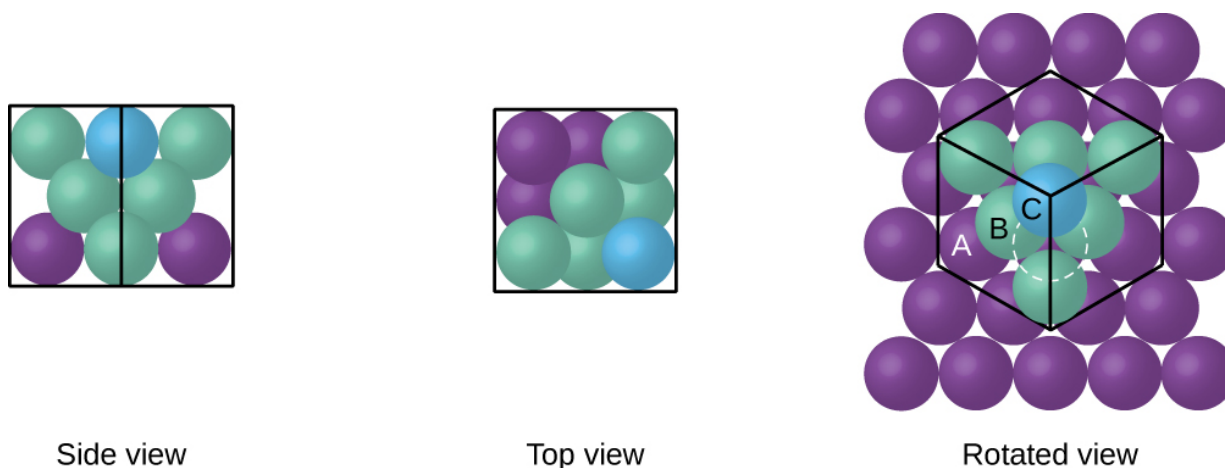
Many other metals, such as aluminum, copper, and lead, crystallize in an arrangement that has a cubic unit cell with atoms at all of the corners and at the centers of each face, as illustrated in [\[link\]](#). This arrangement is called a **face-centered cubic (FCC) solid**. A FCC unit cell contains four atoms: one-eighth of an atom at each of the eight corners ($8 \times \frac{1}{8} = 1$ atom from the corners) and one-half of an atom on each of the six faces ($6 \times \frac{1}{2} = 3$ atoms from the faces). The atoms at the corners touch the atoms in the centers of the adjacent faces along the face diagonals of the cube. Because the atoms are on identical lattice points, they have identical environments.



Face-centered cubic structure

A face-centered cubic solid has atoms at the corners and, as the name implies, at the centers of the faces of its unit cells.

Atoms in an FCC arrangement are packed as closely together as possible, with atoms occupying 74% of the volume. This structure is also called **cubic closest packing (CCP)**. In CCP, there are three repeating layers of hexagonally arranged atoms. Each atom contacts six atoms in its own layer, three in the layer above, and three in the layer below. In this arrangement, each atom touches 12 near neighbors, and therefore has a coordination number of 12. The fact that FCC and CCP arrangements are equivalent may not be immediately obvious, but why they are actually the same structure is illustrated in [\[link\]](#).



Side view

Top view

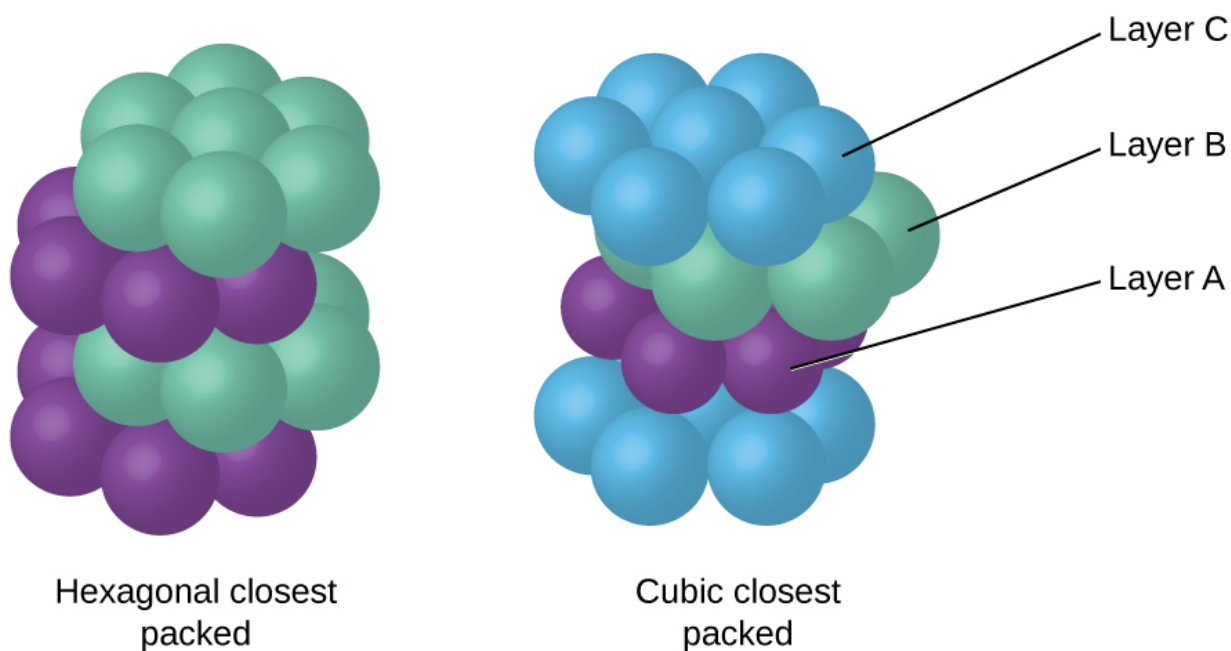
Rotated view

Cubic closest packed structure

A CCP arrangement consists of three repeating layers (ABCABC...) of hexagonally arranged atoms. Atoms in a CCP structure have a coordination number of 12 because they contact six atoms in their layer, plus three atoms in the layer above and three atoms in the layer below. By rotating our perspective, we can see that a CCP structure has a unit cell with a face containing an atom from layer A at one corner, atoms from layer B across a diagonal (at two corners and in the

middle of the face), and an atom from layer C at the remaining corner. This is the same as a face-centered cubic arrangement.

Because closer packing maximizes the overall attractions between atoms and minimizes the total intermolecular energy, the atoms in most metals pack in this manner. We find two types of closest packing in simple metallic crystalline structures: CCP, which we have already encountered, and **hexagonal closest packing (HCP)** shown in [\[link\]](#). Both consist of repeating layers of hexagonally arranged atoms. In both types, a second layer (B) is placed on the first layer (A) so that each atom in the second layer is in contact with three atoms in the first layer. The third layer is positioned in one of two ways. In HCP, atoms in the third layer are directly above atoms in the first layer (i.e., the third layer is also type A), and the stacking consists of alternating type A and type B close-packed layers (i.e., ABABAB...). In CCP, atoms in the third layer are not above atoms in either of the first two layers (i.e., the third layer is type C), and the stacking consists of alternating type A, type B, and type C close-packed layers (i.e., ABCABCABC...). About two-thirds of all metals crystallize in closest-packed arrays with coordination numbers of 12. Metals that crystallize in an HCP structure include Cd, Co, Li, Mg, Na, and Zn, and metals that crystallize in a CCP structure include Ag, Al, Ca, Cu, Ni, Pb, and Pt.



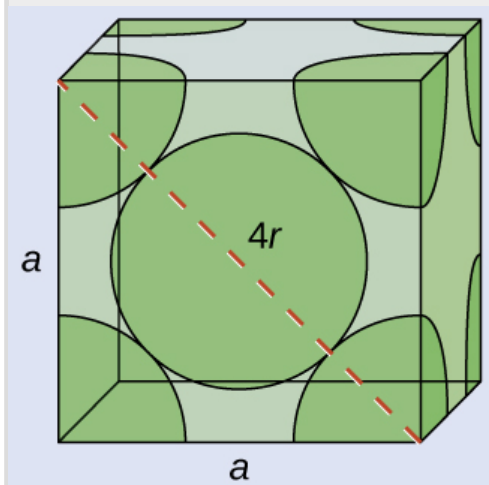
In both types of closest packing, atoms are packed as compactly as possible. Hexagonal closest packing consists of two alternating layers (ABABAB...). Cubic closest packing consists of three alternating layers (ABCABCABC...).

Example:**Calculation of Atomic Radius and Density for Metals, Part 2**

Calcium crystallizes in a face-centered cubic structure. The edge length of its unit cell is 558.8 pm.

(a) What is the atomic radius of Ca in this structure?

(b) Calculate the density of Ca.

Solution

(a) In an FCC structure, Ca atoms contact each other across the diagonal of the face, so the length of the diagonal is equal to four Ca atomic radii ($d = 4r$). Two adjacent edges and the diagonal of the face form a right triangle, with the length of each side equal to 558.8 pm and the length of the hypotenuse equal to four Ca atomic radii:

Equation:

$$a^2 + a^2 = d^2 \rightarrow (558.8 \text{ pm})^2 + (558.8 \text{ pm})^2 = (4r)^2$$

Solving this gives $r = \sqrt{\frac{(558.8 \text{ pm})^2 + (558.8 \text{ pm})^2}{16}} = 197.6 \text{ pm}$ for a Ca radius.

(b) Density is given by $\text{density} = \frac{\text{mass}}{\text{volume}}$. The density of calcium can be found by determining the density of its unit cell: for example, the mass contained within a unit cell divided by the volume of the unit cell. A face-centered Ca unit cell has one-eighth of an atom at each of the eight corners ($8 \times \frac{1}{8} = 1 \text{ atom}$) and one-half of an atom on each of the six faces ($6 \times \frac{1}{2} = 3 \text{ atoms}$), for a total of four atoms in the unit cell.

The mass of the unit cell can be found by:

Equation:

$$1 \text{ Ca unit cell} \times \frac{4 \text{ Ca atoms}}{1 \text{ Ca unit cell}} \times \frac{1 \text{ mol Ca}}{6.022 \times 10^{23} \text{ Ca atoms}} \times \frac{40.078 \text{ g}}{1 \text{ mol Ca}} = 2.662 \times 10^{-22} \text{ g}$$

The volume of a Ca unit cell can be found by:

Equation:

$$V = a^3 = (558.8 \times 10^{-10} \text{ cm})^3 = 1.745 \times 10^{-22} \text{ cm}^3$$

(Note that the edge length was converted from pm to cm to get the usual volume units for density.)

Then, the density of Ca = $\frac{2.662 \times 10^{-22} \text{ g}}{1.745 \times 10^{-22} \text{ cm}^3} = 1.53 \text{ g/cm}^3$

Check Your Learning

Silver crystallizes in an FCC structure. The edge length of its unit cell is 409 pm.

(a) What is the atomic radius of Ag in this structure?

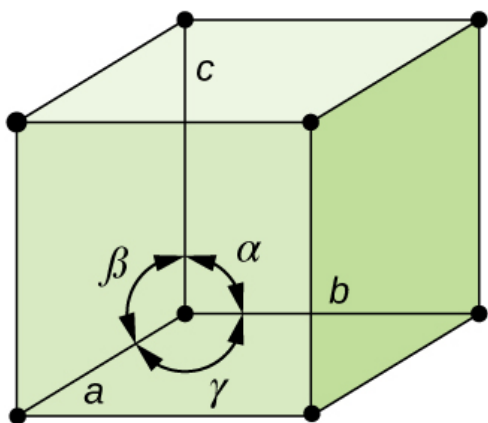
(b) Calculate the density of Ag.

Note:

Answer:

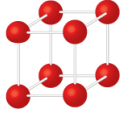
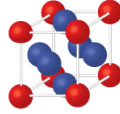
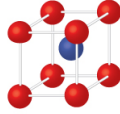
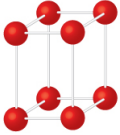
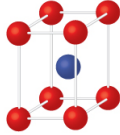
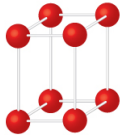
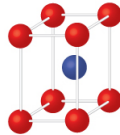
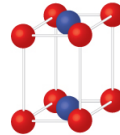
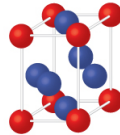
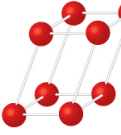
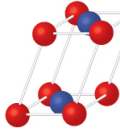
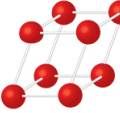
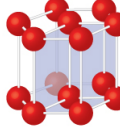
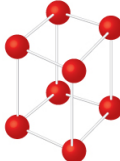
(a) 144 pm; (b) 10.5 g/cm³

In general, a unit cell is defined by the lengths of three axes (a , b , and c) and the angles (α , β , and γ) between them, as illustrated in [\[link\]](#). The axes are defined as being the lengths between points in the space lattice. Consequently, unit cell axes join points with identical environments.



A unit cell is defined by the lengths of its three axes (a , b , and c) and the angles (α , β , and γ) between the axes.

There are seven different lattice systems, some of which have more than one type of lattice, for a total of fourteen different unit cells, which have the shapes shown in [\[link\]](#).

System/Axes/Angles	Unit Cells			
Cubic $a = b = c$ $\alpha = \beta = \gamma = 90^\circ$				
	Simple	Face-centered	Body-centered	
Tetragonal $a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$				
	Simple	Body-centered		
Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$				
	Simple	Body-centered	Base-centered	Face-centered
Monoclinic $a \neq b \neq c$ $\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$				
	Simple	Base-centered		
Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$				
Hexagonal $a = b \neq c$ $\alpha = \beta = 90^\circ; \gamma = 120^\circ$				
Rhombohedral $a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$				

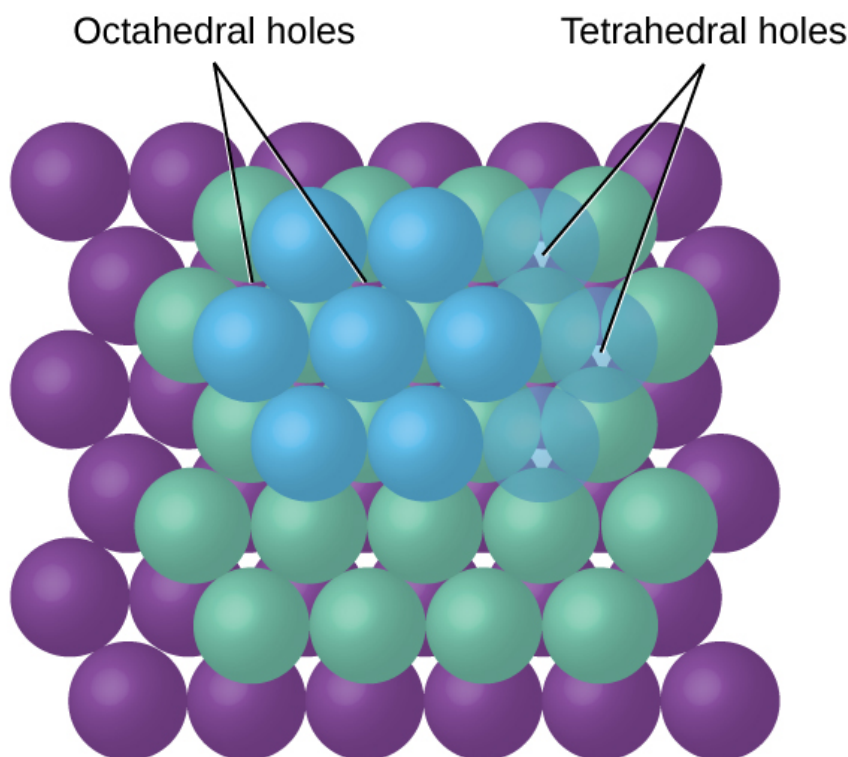
There are seven different lattice systems and 14 different unit cells.

The Structures of Ionic Crystals

Ionic crystals consist of two or more different kinds of ions that usually have different sizes. The packing of these ions into a crystal structure is more complex than the packing of metal atoms that are the same size.

Most monatomic ions behave as charged spheres, and their attraction for ions of opposite charge is the same in every direction. Consequently, stable structures for ionic compounds result (1) when ions of one charge are surrounded by as many ions as possible of the opposite charge and (2) when the cations and anions are in contact with each other. Structures are determined by two principal factors: the relative sizes of the ions and the ratio of the numbers of positive and negative ions in the compound.

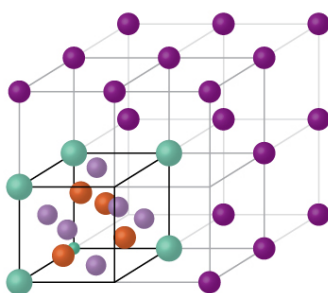
In simple ionic structures, we usually find the anions, which are normally larger than the cations, arranged in a closest-packed array. (As seen previously, additional electrons attracted to the same nucleus make anions larger and fewer electrons attracted to the same nucleus make cations smaller when compared to the atoms from which they are formed.) The smaller cations commonly occupy one of two types of **holes** (or interstices) remaining between the anions. The smaller of the holes is found between three anions in one plane and one anion in an adjacent plane. The four anions surrounding this hole are arranged at the corners of a tetrahedron, so the hole is called a **tetrahedral hole**. The larger type of hole is found at the center of six anions (three in one layer and three in an adjacent layer) located at the corners of an octahedron; this is called an **octahedral hole**. [\[link\]](#) illustrates both of these types of holes.



Cations may occupy two types of holes between anions: octahedral holes or tetrahedral holes.

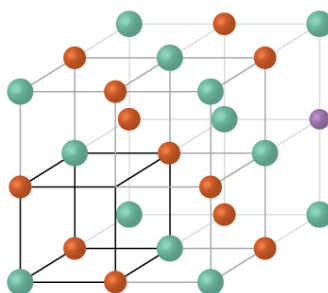
Depending on the relative sizes of the cations and anions, the cations of an ionic compound may occupy tetrahedral or octahedral holes, as illustrated in [\[link\]](#). Relatively small cations occupy tetrahedral holes, and larger cations occupy octahedral holes. If the cations are too large to fit into the

octahedral holes, the anions may adopt a more open structure, such as a simple cubic array. The larger cations can then occupy the larger cubic holes made possible by the more open spacing.



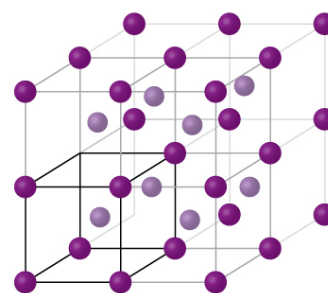
Tetrahedral hole

Cation radius is about 22.5 to 41.4% of the anion radius



Octahedral hole

Cation radius is about 41.4 to 73.2% of the anion radius



Cubic hole

Cation radius is about 73.2 to 100% of the anion radius

A cation's size and the shape of the hole occupied by the compound are directly related.

There are two tetrahedral holes for each anion in either an HCP or CCP array of anions. A compound that crystallizes in a closest-packed array of anions with cations in the tetrahedral holes can have a maximum cation:anion ratio of 2:1; all of the tetrahedral holes are filled at this ratio. Examples include Li_2O , Na_2O , Li_2S , and Na_2S . Compounds with a ratio of less than 2:1 may also crystallize in a closest-packed array of anions with cations in the tetrahedral holes, if the ionic sizes fit. In these compounds, however, some of the tetrahedral holes remain vacant.

Example:

Occupancy of Tetrahedral Holes

Zinc sulfide is an important industrial source of zinc and is also used as a white pigment in paint. Zinc sulfide crystallizes with zinc ions occupying one-half of the tetrahedral holes in a closest-packed array of sulfide ions. What is the formula of zinc sulfide?

Solution

Because there are two tetrahedral holes per anion (sulfide ion) and one-half of these holes are occupied by zinc ions, there must be $\frac{1}{2} \times 2$, or 1, zinc ion per sulfide ion. Thus, the formula is ZnS .

Check Your Learning

Lithium selenide can be described as a closest-packed array of selenide ions with lithium ions in all of the tetrahedral holes. What is the formula of lithium selenide?

Note:

Answer:

Li_2Se

The ratio of octahedral holes to anions in either an HCP or CCP structure is 1:1. Thus, compounds with cations in octahedral holes in a closest-packed array of anions can have a maximum cation:anion ratio of 1:1. In NiO, MnS, NaCl, and KH, for example, all of the octahedral holes are filled. Ratios of less than 1:1 are observed when some of the octahedral holes remain empty.

Example:**Stoichiometry of Ionic Compounds**

Sapphire is aluminum oxide. Aluminum oxide crystallizes with aluminum ions in two-thirds of the octahedral holes in a closest-packed array of oxide ions. What is the formula of aluminum oxide?

Solution

Because there is one octahedral hole per anion (oxide ion) and only two-thirds of these holes are occupied, the ratio of aluminum to oxygen must be $\frac{2}{3}:1$, which would give $\text{Al}_{2/3}\text{O}$. The simplest whole number ratio is 2:3, so the formula is Al_2O_3 .

Check Your Learning

The white pigment titanium oxide crystallizes with titanium ions in one-half of the octahedral holes in a closest-packed array of oxide ions. What is the formula of titanium oxide?

Note:**Answer:**

TiO_2

In a simple cubic array of anions, there is one cubic hole that can be occupied by a cation for each anion in the array. In CsCl, and in other compounds with the same structure, all of the cubic holes are occupied. Half of the cubic holes are occupied in SrH_2 , UO_2 , SrCl_2 , and CaF_2 .

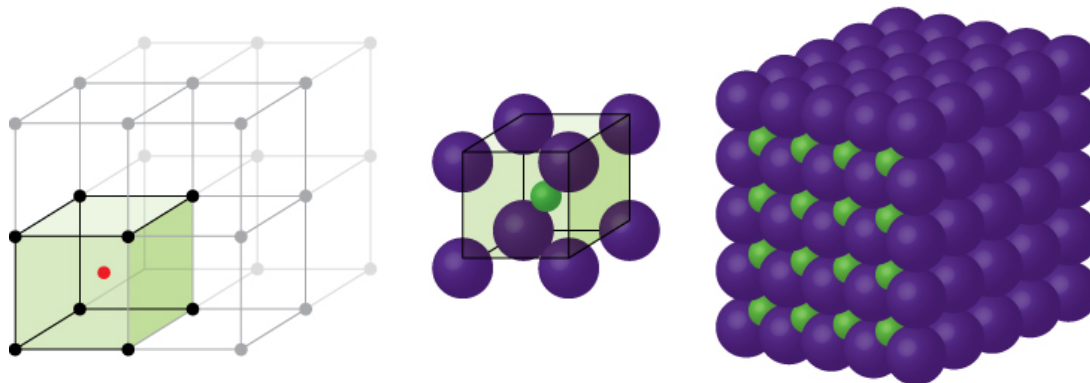
Different types of ionic compounds often crystallize in the same structure when the relative sizes of their ions and their stoichiometries (the two principal features that determine structure) are similar.

Unit Cells of Ionic Compounds

Many ionic compounds crystallize with cubic unit cells, and we will use these compounds to describe the general features of ionic structures.

When an ionic compound is composed of cations and anions of similar size in a 1:1 ratio, it typically forms a simple cubic structure. Cesium chloride, CsCl, (illustrated in [\[link\]](#)) is an example of this, with Cs^+ and Cl^- having radii of 174 pm and 181 pm, respectively. We can think of this as chloride ions forming a simple cubic unit cell, with a cesium ion in the center; or as cesium ions forming a unit cell with a chloride ion in the center; or as simple cubic unit cells formed by Cs^+ ions overlapping unit cells formed by Cl^- ions. Cesium ions and chloride ions touch along the body diagonals of the unit

cells. One cesium ion and one chloride ion are present per unit cell, giving the 1:1 stoichiometry required by the formula for cesium chloride. Note that there is no lattice point in the center of the cell, and CsCl is not a BCC structure because a cesium ion is not identical to a chloride ion.

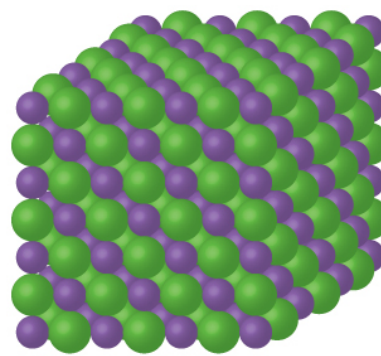
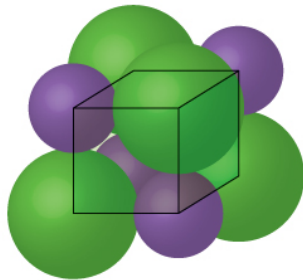
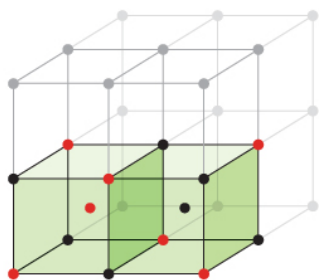


Simple cubic structure

Ionic compounds with similar-sized cations and anions, such as CsCl, usually form a simple cubic structure. They can be described by unit cells with either cations at the corners or anions at the corners.

We have said that the location of lattice points is arbitrary. This is illustrated by an alternate description of the CsCl structure in which the lattice points are located in the centers of the cesium ions. In this description, the cesium ions are located on the lattice points at the corners of the cell, and the chloride ion is located at the center of the cell. The two unit cells are different, but they describe identical structures.

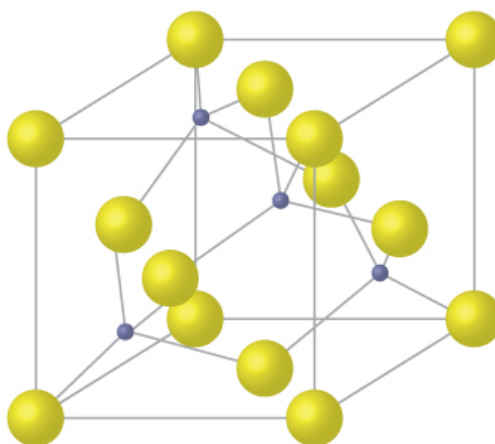
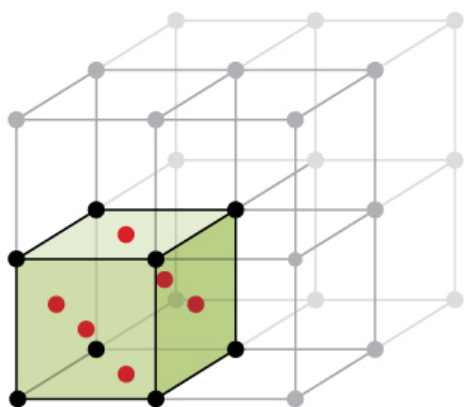
When an ionic compound is composed of a 1:1 ratio of cations and anions that differ significantly in size, it typically crystallizes with an FCC unit cell, like that shown in [\[link\]](#). Sodium chloride, NaCl, is an example of this, with Na^+ and Cl^- having radii of 102 pm and 181 pm, respectively. We can think of this as chloride ions forming an FCC cell, with sodium ions located in the octahedral holes in the middle of the cell edges and in the center of the cell. The sodium and chloride ions touch each other along the cell edges. The unit cell contains four sodium ions and four chloride ions, giving the 1:1 stoichiometry required by the formula, NaCl.



Face-centered simple cubic structure

Ionic compounds with anions that are much larger than cations, such as NaCl, usually form an FCC structure. They can be described by FCC unit cells with cations in the octahedral holes.

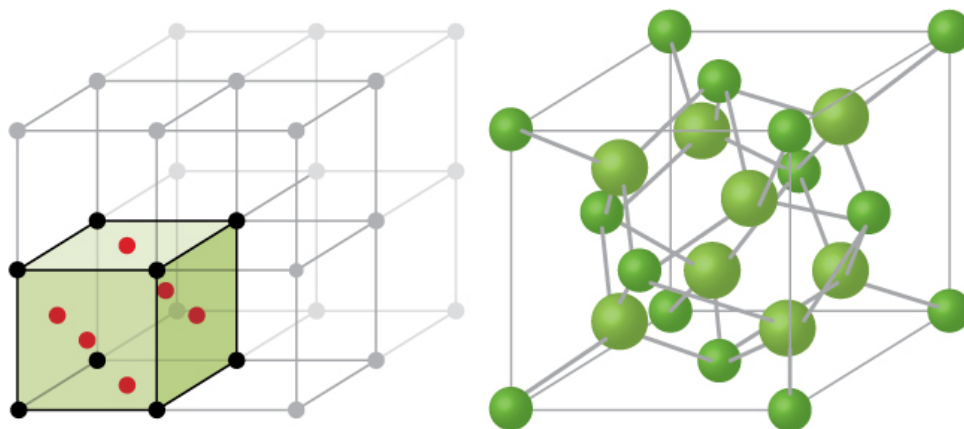
The cubic form of zinc sulfide, zinc blende, also crystallizes in an FCC unit cell, as illustrated in [\[link\]](#). This structure contains sulfide ions on the lattice points of an FCC lattice. (The arrangement of sulfide ions is identical to the arrangement of chloride ions in sodium chloride.) The radius of a zinc ion is only about 40% of the radius of a sulfide ion, so these small Zn^{2+} ions are located in alternating tetrahedral holes, that is, in one half of the tetrahedral holes. There are four zinc ions and four sulfide ions in the unit cell, giving the empirical formula ZnS.



ZnS face-centered unit cell

ZnS, zinc sulfide (or zinc blende) forms an FCC unit cell with sulfide ions at the lattice points and much smaller zinc ions occupying half of the tetrahedral holes in the structure.

A calcium fluoride unit cell, like that shown in [\[link\]](#), is also an FCC unit cell, but in this case, the cations are located on the lattice points; equivalent calcium ions are located on the lattice points of an FCC lattice. All of the tetrahedral sites in the FCC array of calcium ions are occupied by fluoride ions. There are four calcium ions and eight fluoride ions in a unit cell, giving a calcium:fluorine ratio of 1:2, as required by the chemical formula, CaF_2 . Close examination of [\[link\]](#) will reveal a simple cubic array of fluoride ions with calcium ions in one half of the cubic holes. The structure cannot be described in terms of a **space lattice** of points on the fluoride ions because the fluoride ions do not all have identical environments. The orientation of the four calcium ions about the fluoride ions differs.



CaF_2 face-centered unit cell

Calcium fluoride, CaF_2 , forms an FCC unit cell with calcium ions (green) at the lattice points and fluoride ions (red) occupying all of the tetrahedral sites between them.

Calculation of Ionic Radii

If we know the edge length of a unit cell of an ionic compound and the position of the ions in the cell, we can calculate ionic radii for the ions in the compound if we make assumptions about individual ionic shapes and contacts.

Example:

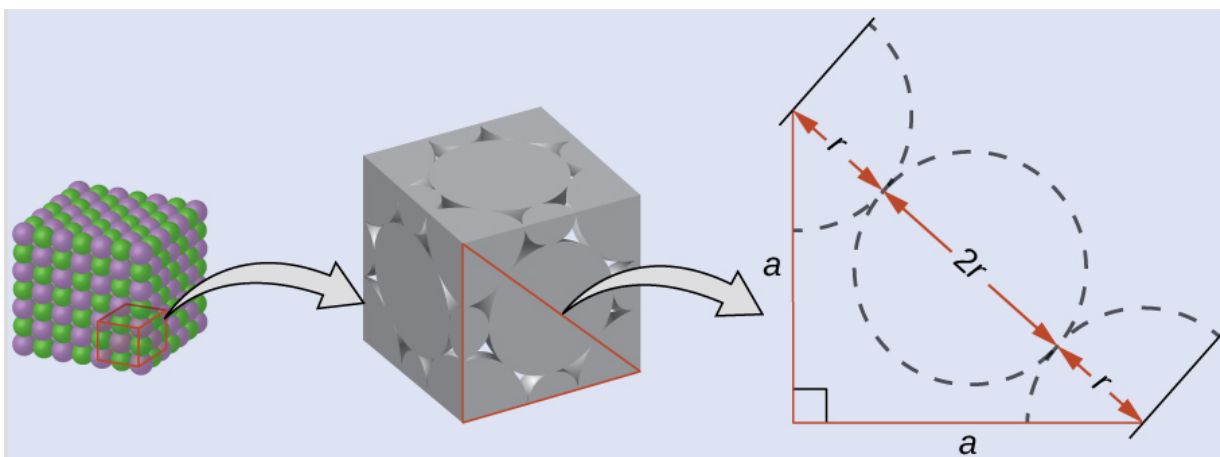
Calculation of Ionic Radii

The edge length of the unit cell of LiCl (NaCl-like structure, FCC) is 0.514 nm or 5.14 Å. Assuming that the lithium ion is small enough so that the chloride ions are in contact, as in [\[link\]](#), calculate the ionic radius for the chloride ion.

Note: The length unit angstrom, Å, is often used to represent atomic-scale dimensions and is equivalent to 10^{-10} m.

Solution

On the face of a LiCl unit cell, chloride ions contact each other across the diagonal of the face:



Drawing a right triangle on the face of the unit cell, we see that the length of the diagonal is equal to four chloride radii (one radius from each corner chloride and one diameter—which equals two radii—from the chloride ion in the center of the face), so $d = 4r$. From the Pythagorean theorem, we have:

Equation:

$$a^2 + a^2 = d^2$$

which yields:

Equation:

$$(0.514 \text{ nm})^2 + (0.514 \text{ nm})^2 = (4r)^2 = 16r^2$$

Solving this gives:

Equation:

$$r = \sqrt{\frac{(0.514 \text{ nm})^2 + (0.514 \text{ nm})^2}{16}} = 0.182 \text{ nm (1.82 \AA)} \text{ for a Cl}^- \text{ radius.}$$

Check Your Learning

The edge length of the unit cell of KCl (NaCl-like structure, FCC) is 6.28 Å. Assuming anion-cation contact along the cell edge, calculate the radius of the potassium ion. The radius of the chloride ion is 1.82 Å.

Note:

Answer:

The radius of the potassium ion is 1.33 Å.

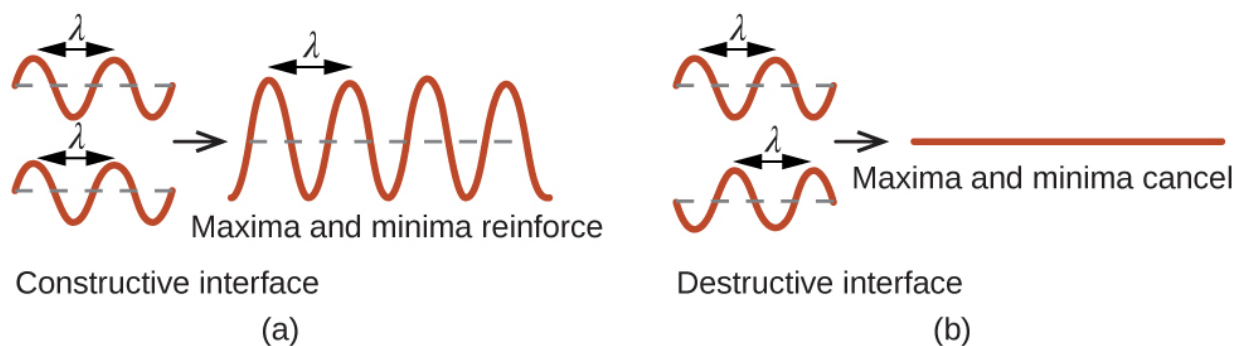
It is important to realize that values for ionic radii calculated from the edge lengths of unit cells depend on numerous assumptions, such as a perfect spherical shape for ions, which are

approximations at best. Hence, such calculated values are themselves approximate and comparisons cannot be pushed too far. Nevertheless, this method has proved useful for calculating ionic radii from experimental measurements such as X-ray crystallographic determinations.

X-Ray Crystallography

The size of the unit cell and the arrangement of atoms in a crystal may be determined from measurements of the *diffraction* of X-rays by the crystal, termed **X-ray crystallography**. **Diffraction** is the change in the direction of travel experienced by an electromagnetic wave when it encounters a physical barrier whose dimensions are comparable to those of the wavelength of the light. X-rays are electromagnetic radiation with wavelengths about as long as the distance between neighboring atoms in crystals (on the order of a few Å).

When a beam of monochromatic X-rays strikes a crystal, its rays are scattered in all directions by the atoms within the crystal. When scattered waves traveling in the same direction encounter one another, they undergo *interference*, a process by which the waves combine to yield either an increase or a decrease in amplitude (intensity) depending upon the extent to which the combining waves' maxima are separated (see [\[link\]](#)).



Light waves occupying the same space experience interference, combining to yield waves of greater (a) or lesser (b) intensity, depending upon the separation of their maxima and minima.

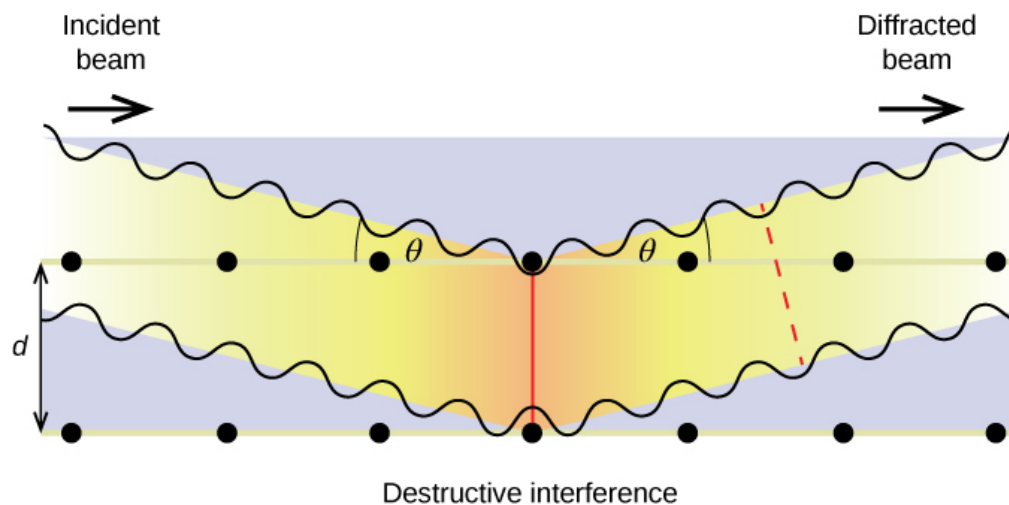
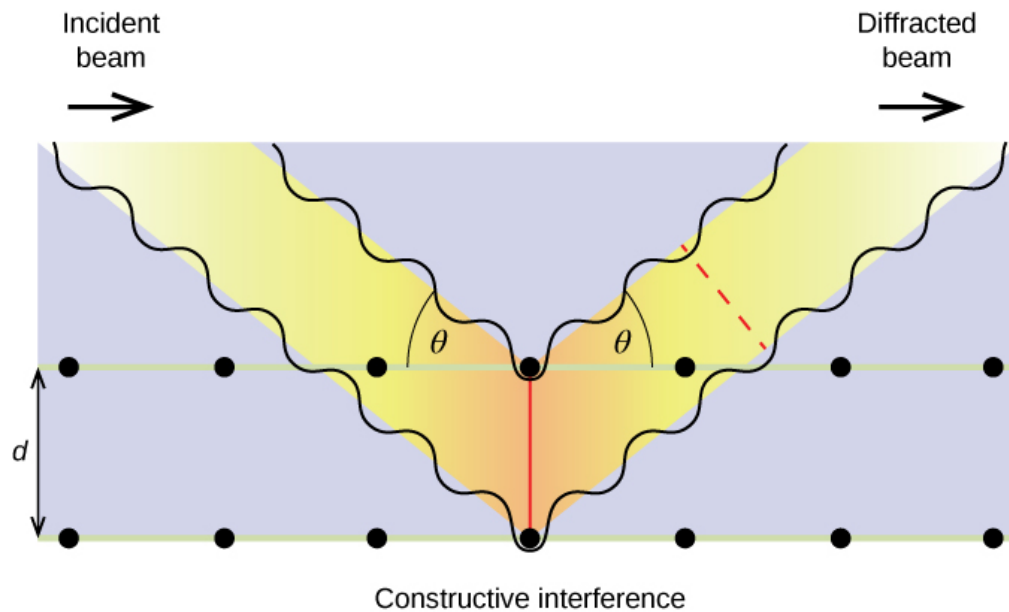
When X-rays of a certain wavelength, λ , are scattered by atoms in adjacent crystal planes separated by a distance, d , they may undergo constructive interference when the difference between the distances traveled by the two waves prior to their combination is an integer factor, n , of the wavelength. This condition is satisfied when the angle of the diffracted beam, θ , is related to the wavelength and interatomic distance by the equation:

Equation:

$$n\lambda = 2d \sin \theta$$

This relation is known as the **Bragg equation** in honor of W. H. Bragg, the English physicist who first explained this phenomenon. [\[link\]](#) illustrates two examples of diffracted waves from the same two crystal planes. The figure on the left depicts waves diffracted at the Bragg angle, resulting in

constructive interference, while that on the right shows diffraction and a different angle that does not satisfy the Bragg condition, resulting in destructive interference.



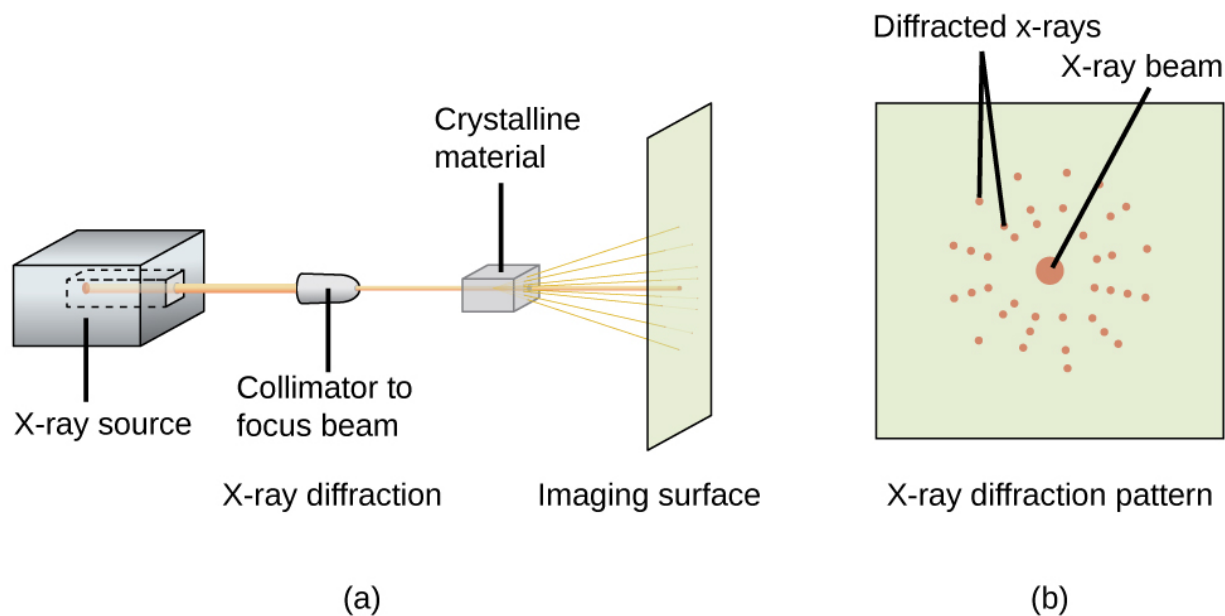
The diffraction of X-rays scattered by the atoms within a crystal permits the determination of the distance between the atoms. The top image depicts constructive interference between two scattered waves and a resultant diffracted wave of high intensity. The bottom image depicts destructive interference and a low intensity diffracted wave.

Note:



Visit this [site](#) for more details on the Bragg equation and a simulator that allows you to explore the effect of each variable on the intensity of the diffracted wave.

An X-ray diffractometer, such as the one illustrated in [\[link\]](#), may be used to measure the angles at which X-rays are diffracted when interacting with a crystal as described earlier. From such measurements, the Bragg equation may be used to compute distances between atoms as demonstrated in the following example exercise.



(a) In a diffractometer, a beam of X-rays strikes a crystalline material, producing (b) an X-ray diffraction pattern that can be analyzed to determine the crystal structure.

Example:

Using the Bragg Equation

In a diffractometer, X-rays with a wavelength of 0.1315 nm were used to produce a diffraction pattern for copper. The first order diffraction ($n = 1$) occurred at an angle $\theta = 25.25^\circ$. Determine the spacing between the diffracting planes in copper.

Solution

The distance between the planes is found by solving the Bragg equation, $n\lambda = 2d \sin \theta$, for d .

This gives: $d = \frac{n\lambda}{2 \sin \theta} = \frac{1(0.1315 \text{ nm})}{2 \sin (25.25^\circ)} = 0.154 \text{ nm}$

Check Your Learning

A crystal with spacing between planes equal to 0.394 nm diffracts X-rays with a wavelength of 0.147 nm. What is the angle for the first order diffraction?

Note:**Answer:**

21.9°.

Note:**X-ray Crystallographer Rosalind Franklin**

The discovery of the structure of DNA in 1953 by Francis Crick and James Watson is one of the great achievements in the history of science. They were awarded the 1962 Nobel Prize in Physiology or Medicine, along with Maurice Wilkins, who provided experimental proof of DNA's structure. British chemist Rosalind Franklin made invaluable contributions to this monumental achievement through her work in measuring X-ray diffraction images of DNA. Early in her career, Franklin's research on the structure of coals proved helpful to the British war effort. After shifting her focus to biological systems in the early 1950s, Franklin and doctoral student Raymond Gosling discovered that DNA consists of two forms: a long, thin fiber formed when wet (type "B") and a short, wide fiber formed when dried (type "A"). Her X-ray diffraction images of DNA ([link](#)) provided the crucial information that allowed Watson and Crick to confirm that DNA forms a double helix, and to determine details of its size and structure. Franklin also conducted pioneering research on viruses and the RNA that contains their genetic information, uncovering new information that radically changed the body of knowledge in the field. After developing ovarian cancer, Franklin continued to work until her death in 1958 at age 37. Among many posthumous recognitions of her work, the Chicago Medical School of Finch University of Health Sciences changed its name to the Rosalind Franklin University of Medicine and Science in 2004, and adopted an image of her famous X-ray diffraction image of DNA as its official university logo.



This illustration shows an X-ray diffraction image similar to the one Franklin found in her research.
(credit: National Institutes of Health)

Key Concepts and Summary

The structures of crystalline metals and simple ionic compounds can be described in terms of packing of spheres. Metal atoms can pack in hexagonal closest-packed structures, cubic closest-packed structures, body-centered structures, and simple cubic structures. The anions in simple ionic structures commonly adopt one of these structures, and the cations occupy the spaces remaining between the anions. Small cations usually occupy tetrahedral holes in a closest-packed array of anions. Larger cations usually occupy octahedral holes. Still larger cations can occupy cubic holes in a simple cubic array of anions. The structure of a solid can be described by indicating the size and shape of a unit cell and the contents of the cell. The type of structure and dimensions of the unit cell can be determined by X-ray diffraction measurements.

Key Equations

- $n\lambda = 2d \sin \theta$

Chemistry End of Chapter Exercises

Exercise:

Problem:

Describe the crystal structure of iron, which crystallizes with two equivalent metal atoms in a cubic unit cell.

Solution:

The structure of this low-temperature form of iron (below 910 °C) is body-centered cubic. There is one-eighth atom at each of the eight corners of the cube and one atom in the center of the cube.

Exercise:**Problem:**

Describe the crystal structure of Pt, which crystallizes with four equivalent metal atoms in a cubic unit cell.

Exercise:**Problem:**

What is the coordination number of a chromium atom in the body-centered cubic structure of chromium?

Solution:

eight

Exercise:**Problem:**

What is the coordination number of an aluminum atom in the face-centered cubic structure of aluminum?

Exercise:**Problem:**

Cobalt metal crystallizes in a hexagonal closest packed structure. What is the coordination number of a cobalt atom?

Solution:

12

Exercise:**Problem:**

Nickel metal crystallizes in a cubic closest packed structure. What is the coordination number of a nickel atom?

Exercise:

Problem:

Tungsten crystallizes in a body-centered cubic unit cell with an edge length of 3.165 Å.

- (a) What is the atomic radius of tungsten in this structure?
 - (b) Calculate the density of tungsten.
-

Solution:

- (a) 1.370 Å; (b) 19.26 g/cm

Exercise:**Problem:**

Platinum (atomic radius = 1.38 Å) crystallizes in a cubic closely packed structure. Calculate the edge length of the face-centered cubic unit cell and the density of platinum.

Exercise:

Problem: Barium crystallizes in a body-centered cubic unit cell with an edge length of 5.025 Å

- (a) What is the atomic radius of barium in this structure?
 - (b) Calculate the density of barium.
-

Solution:

- (a) 2.176 Å; (b) 3.595 g/cm³

Exercise:**Problem:**

Aluminum (atomic radius = 1.43 Å) crystallizes in a cubic closely packed structure. Calculate the edge length of the face-centered cubic unit cell and the density of aluminum.

Exercise:**Problem:**

The density of aluminum is 2.7 g/cm³; that of silicon is 2.3 g/cm³. Explain why Si has the lower density even though it has heavier atoms.

Solution:

The crystal structure of Si shows that it is less tightly packed (coordination number 4) in the solid than Al (coordination number 12).

Exercise:

Problem:

The free space in a metal may be found by subtracting the volume of the atoms in a unit cell from the volume of the cell. Calculate the percentage of free space in each of the three cubic lattices if all atoms in each are of equal size and touch their nearest neighbors. Which of these structures represents the most efficient packing? That is, which packs with the least amount of unused space?

Exercise:**Problem:**

Cadmium sulfide, sometimes used as a yellow pigment by artists, crystallizes with cadmium, occupying one-half of the tetrahedral holes in a closest packed array of sulfide ions. What is the formula of cadmium sulfide? Explain your answer.

Solution:

In a closest-packed array, two tetrahedral holes exist for each anion. If only half the tetrahedral holes are occupied, the numbers of anions and cations are equal. The formula for cadmium sulfide is CdS.

Exercise:**Problem:**

A compound of cadmium, tin, and phosphorus is used in the fabrication of some semiconductors. It crystallizes with cadmium occupying one-fourth of the tetrahedral holes and tin occupying one-fourth of the tetrahedral holes in a closest packed array of phosphide ions. What is the formula of the compound? Explain your answer.

Exercise:**Problem:**

What is the formula of the magnetic oxide of cobalt, used in recording tapes, that crystallizes with cobalt atoms occupying one-eighth of the tetrahedral holes and one-half of the octahedral holes in a closely packed array of oxide ions?

Solution:**Exercise:****Problem:**

A compound containing zinc, aluminum, and sulfur crystallizes with a closest-packed array of sulfide ions. Zinc ions are found in one-eighth of the tetrahedral holes and aluminum ions in one-half of the octahedral holes. What is the empirical formula of the compound?

Exercise:

Problem:

A compound of thallium and iodine crystallizes in a simple cubic array of iodide ions with thallium ions in all of the cubic holes. What is the formula of this iodide? Explain your answer.

Solution:

In a simple cubic array, only one cubic hole can be occupied by a cation for each anion in the array. The ratio of thallium to iodide must be 1:1; therefore, the formula for thallium is TlI.

Exercise:**Problem:**

Which of the following elements reacts with sulfur to form a solid in which the sulfur atoms form a closest-packed array with all of the octahedral holes occupied: Li, Na, Be, Ca, or Al?

Exercise:**Problem:**

What is the percent by mass of titanium in rutile, a mineral that contains titanium and oxygen, if structure can be described as a closest packed array of oxide ions with titanium ions in one-half of the octahedral holes? What is the oxidation number of titanium?

Solution:

59.95%; The oxidation number of titanium is +4.

Exercise:**Problem:**

Explain why the chemically similar alkali metal chlorides NaCl and CsCl have different structures, whereas the chemically different NaCl and MnS have the same structure.

Exercise:**Problem:**

As minerals were formed from the molten magma, different ions occupied the same sites in the crystals. Lithium often occurs along with magnesium in minerals despite the difference in the charge on their ions. Suggest an explanation.

Solution:

Both ions are close in size: Mg, 0.65; Li, 0.60. This similarity allows the two to interchange rather easily. The difference in charge is generally compensated by the switch of Si^{4+} for Al^{3+} .

Exercise:**Problem:**

Rubidium iodide crystallizes with a cubic unit cell that contains iodide ions at the corners and a rubidium ion in the center. What is the formula of the compound?

Exercise:

Problem:

One of the various manganese oxides crystallizes with a cubic unit cell that contains manganese ions at the corners and in the center. Oxide ions are located at the center of each edge of the unit cell. What is the formula of the compound?

Solution:**Exercise:****Problem:**

NaH crystallizes with the same crystal structure as NaCl. The edge length of the cubic unit cell of NaH is 4.880 Å.

- (a) Calculate the ionic radius of H^- . (The ionic radius of Li^+ is 0.095 Å.)
- (b) Calculate the density of NaH.

Exercise:**Problem:**

Thallium(I) iodide crystallizes with the same structure as CsCl. The edge length of the unit cell of TlI is 4.20 Å. Calculate the ionic radius of Tl^+ . (The ionic radius of I^- is 2.16 Å.)

Solution:

$$1.48 \text{ Å}$$

Exercise:**Problem:**

A cubic unit cell contains manganese ions at the corners and fluoride ions at the center of each edge.

- (a) What is the empirical formula of this compound? Explain your answer.
- (b) What is the coordination number of the Mn^{3+} ion?
- (c) Calculate the edge length of the unit cell if the radius of a Mn^{3+} ion is 0.65 Å.
- (d) Calculate the density of the compound.

Exercise:**Problem:**

What is the spacing between crystal planes that diffract X-rays with a wavelength of 1.541 nm at an angle θ of 15.55° (first order reflection)?

Solution:

2.874 Å

Exercise:

Problem:

A diffractometer using X-rays with a wavelength of 0.2287 nm produced first-order diffraction peak for a crystal angle $\theta = 16.21^\circ$. Determine the spacing between the diffracting planes in this crystal.

Exercise:

Problem:

A metal with spacing between planes equal to 0.4164 nm diffracts X-rays with a wavelength of 0.2879 nm. What is the diffraction angle for the first order diffraction peak?

Solution:

20.2°

Exercise:

Problem:

Gold crystallizes in a face-centered cubic unit cell. The second-order reflection ($n = 2$) of X-rays for the planes that make up the tops and bottoms of the unit cells is at $\theta = 22.20^\circ$. The wavelength of the X-rays is 1.54 Å. What is the density of metallic gold?

Exercise:

Problem:

When an electron in an excited molybdenum atom falls from the L to the K shell, an X-ray is emitted. These X-rays are diffracted at an angle of 7.75° by planes with a separation of 2.64 Å. What is the difference in energy between the K shell and the L shell in molybdenum assuming a first-order diffraction?

Solution:

1.74×10^4 eV

Glossary

body-centered cubic (BCC) solid

crystalline structure that has a cubic unit cell with lattice points at the corners and in the center of the cell

body-centered cubic unit cell

simplest repeating unit of a body-centered cubic crystal; it is a cube containing lattice points at each corner and in the center of the cube

Bragg equation

equation that relates the angles at which X-rays are diffracted by the atoms within a crystal

coordination number

number of atoms closest to any given atom in a crystal or to the central metal atom in a complex

cubic closest packing (CCP)

crystalline structure in which planes of closely packed atoms or ions are stacked as a series of three alternating layers of different relative orientations (ABC)

diffraction

redirection of electromagnetic radiation that occurs when it encounters a physical barrier of appropriate dimensions

face-centered cubic (FCC) solid

crystalline structure consisting of a cubic unit cell with lattice points on the corners and in the center of each face

face-centered cubic unit cell

simplest repeating unit of a face-centered cubic crystal; it is a cube containing lattice points at each corner and in the center of each face

hexagonal closest packing (HCP)

crystalline structure in which close packed layers of atoms or ions are stacked as a series of two alternating layers of different relative orientations (AB)

hole

(also, interstice) space between atoms within a crystal

isomorphous

possessing the same crystalline structure

octahedral hole

open space in a crystal at the center of six particles located at the corners of an octahedron

simple cubic unit cell

(also, primitive cubic unit cell) unit cell in the simple cubic structure

simple cubic structure

crystalline structure with a cubic unit cell with lattice points only at the corners

space lattice

all points within a crystal that have identical environments

tetrahedral hole

tetrahedral space formed by four atoms or ions in a crystal

unit cell

smallest portion of a space lattice that is repeated in three dimensions to form the entire lattice

X-ray crystallography

experimental technique for determining distances between atoms in a crystal by measuring the angles at which X-rays are diffracted when passing through the crystal

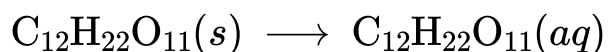
The Dissolution Process

By the end of this section, you will be able to:

- Describe the basic properties of solutions and how they form
- Predict whether a given mixture will yield a solution based on molecular properties of its components
- Explain why some solutions either produce or absorb heat when they form

An earlier chapter of this text introduced *solutions*, defined as homogeneous mixtures of two or more substances. Often, one component of a solution is present at a significantly greater concentration, in which case it is called the *solvent*. The other components of the solution present in relatively lesser concentrations are called *solutes*. Sugar is a covalent solid composed of sucrose molecules, $C_{12}H_{22}O_{11}$. When this compound dissolves in water, its molecules become uniformly distributed among the molecules of water:

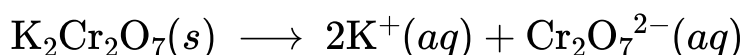
Equation:



The subscript “aq” in the equation signifies that the sucrose molecules are solutes and are therefore *individually dispersed* throughout the *aqueous solution* (water is the solvent). Although sucrose molecules are heavier than water molecules, they remain dispersed throughout the solution; gravity does not cause them to “settle out” over time.

Potassium dichromate, $K_2Cr_2O_7$, is an ionic compound composed of colorless potassium ions, K^+ , and orange dichromate ions, $Cr_2O_7^{2-}$. When a small amount of solid potassium dichromate is added to water, the compound dissolves and dissociates to yield potassium ions and dichromate ions uniformly distributed throughout the mixture ([\[link\]](#)), as indicated in this equation:

Equation:



As with the mixture of sugar and water, this mixture is also an aqueous solution. Its solutes, potassium and dichromate ions, remain individually dispersed among the solvent (water) molecules.



When potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) is mixed with water, it forms a homogeneous orange solution. (credit: modification of work by Mark Ott)

Note:



Visit this [virtual lab](#) to view simulations of the dissolution of common covalent and ionic substances (sugar and salt) in water.

Water is used so often as a solvent that the word solution has come to imply an aqueous solution to many people. However, almost any gas, liquid, or solid can act as a solvent. Many **alloys** are solid solutions of one metal dissolved in another; for example, US five-cent coins contain nickel dissolved in copper. Air is a gaseous solution, a homogeneous mixture of nitrogen, oxygen, and several other gases. Oxygen (a gas), alcohol (a

liquid), and sugar (a solid) all dissolve in water (a liquid) to form liquid solutions. [\[link\]](#) gives examples of several different solutions and the phases of the solutes and solvents.

Different Types of Solutions		
Solution	Solute	Solvent
air	$O_2(g)$	$N_2(g)$
soft drinks [footnote] If bubbles of gas are observed within the liquid, the mixture is not homogeneous and, thus, not a solution.	$CO_2(g)$	$H_2O(l)$
hydrogen in palladium	$H_2(g)$	$Pd(s)$
rubbing alcohol	$H_2O(l)$	$C_3H_8O(l)$ (2-propanol)
saltwater	$NaCl(s)$	$H_2O(l)$
brass	$Zn(s)$	$Cu(s)$

Solutions exhibit these defining traits:

- They are homogeneous; that is, after a solution is mixed, it has the same composition at all points throughout (its composition is uniform).
- The physical state of a solution—solid, liquid, or gas—is typically the same as that of the solvent, as demonstrated by the examples in [\[link\]](#).

- The components of a solution are dispersed on a molecular scale; that is, they consist of a mixture of separated molecules, atoms, and/or ions.
- The dissolved solute in a solution will not settle out or separate from the solvent.
- The composition of a solution, or the concentrations of its components, can be varied continuously, within limits.

The Formation of Solutions

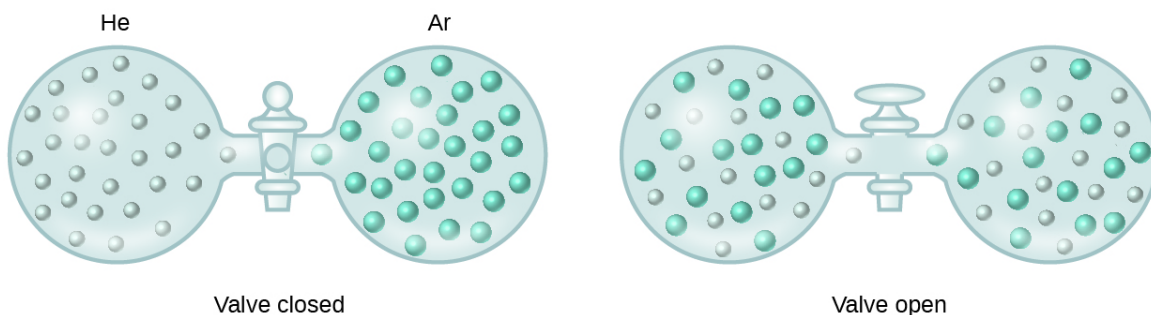
The formation of a solution is an example of a **spontaneous process**, a process that occurs under specified conditions without the requirement of energy from some external source. Sometimes we stir a mixture to speed up the dissolution process, but this is not necessary; a homogeneous solution would form if we waited long enough. The topic of spontaneity is critically important to the study of chemical thermodynamics and is treated more thoroughly in a later chapter of this text. For purposes of this chapter's discussion, it will suffice to consider two criteria that *favor*, but do not guarantee, the spontaneous formation of a solution:

1. a decrease in the internal energy of the system (an exothermic change, as discussed in the previous chapter on thermochemistry)
2. an increase in the disorder in the system (which indicates an increase in the *entropy* of the system, as you will learn about in the later chapter on thermodynamics)

In the process of dissolution, an internal energy change often, but not always, occurs as heat is absorbed or evolved. An increase in disorder always results when a solution forms.

When the strengths of the intermolecular forces of attraction between solute and solvent species in a solution are no different than those present in the separated components, the solution is formed with no accompanying energy change. Such a solution is called an **ideal solution**. A mixture of ideal gases (or gases such as helium and argon, which closely approach ideal behavior) is an example of an ideal solution, since the entities comprising these gases experience no significant intermolecular attractions.

When containers of helium and argon are connected, the gases spontaneously mix due to diffusion and form a solution ([\[link\]](#)). The formation of this solution clearly involves an increase in disorder, since the helium and argon atoms occupy a volume twice as large as that which each occupied before mixing.

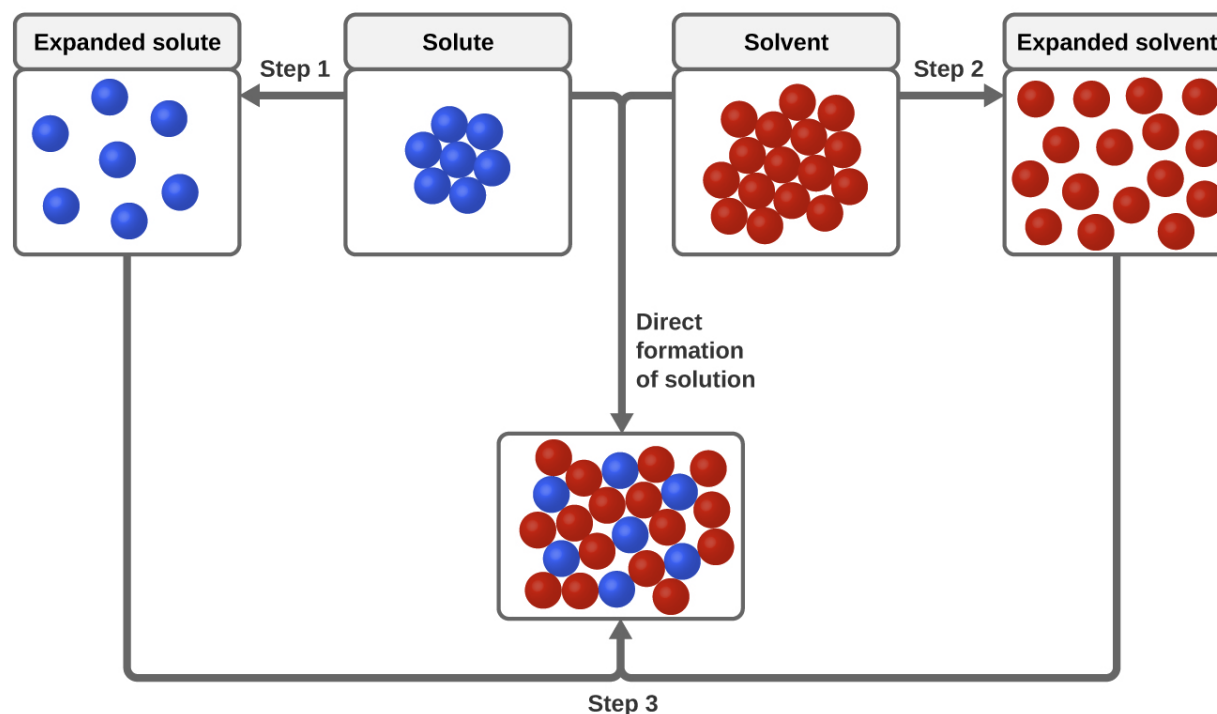


Samples of helium and argon spontaneously mix to give a solution in which the disorder of the atoms of the two gases is increased.

Ideal solutions may also form when structurally similar liquids are mixed. For example, mixtures of the alcohols methanol (CH_3OH) and ethanol ($\text{C}_2\text{H}_5\text{OH}$) form ideal solutions, as do mixtures of the hydrocarbons pentane, C_5H_{12} , and hexane, C_6H_{14} . Placing methanol and ethanol, or pentane and hexane, in the bulbs shown in [\[link\]](#) will result in the same diffusion and subsequent mixing of these liquids as is observed for the He and Ar gases (although at a much slower rate), yielding solutions with no significant change in energy. Unlike a mixture of gases, however, the components of these liquid-liquid solutions do, indeed, experience intermolecular attractive forces. But since the molecules of the two substances being mixed are structurally very similar, the intermolecular attractive forces between like and unlike molecules are essentially the same, and the dissolution process, therefore, does not entail any appreciable increase or decrease in energy. These examples illustrate how diffusion alone can provide the driving force required to cause the spontaneous formation of a solution. In some cases, however, the relative magnitudes of

intermolecular forces of attraction between solute and solvent species may prevent dissolution.

Three types of intermolecular attractive forces are relevant to the dissolution process: solute-solute, solvent-solvent, and solute-solvent. As illustrated in [\[link\]](#), the formation of a solution may be viewed as a stepwise process in which energy is consumed to overcome solute-solute and solvent-solvent attractions (endothermic processes) and released when solute-solvent attractions are established (an exothermic process referred to as **solvation**). The relative magnitudes of the energy changes associated with these stepwise processes determine whether the dissolution process overall will release or absorb energy. In some cases, solutions do not form because the energy required to separate solute and solvent species is so much greater than the energy released by solvation.



This schematic representation of dissolution shows a stepwise process involving the endothermic separation of solute and solvent species

(Steps 1 and 2) and exothermic solvation (Step 3).

For example, cooking oils and water will not mix to any appreciable extent to yield solutions ([\[link\]](#)). Hydrogen bonding is the dominant intermolecular attractive force present in liquid water; the nonpolar hydrocarbon molecules of cooking oils are not capable of hydrogen bonding, instead being held together by dispersion forces. Forming an oil-water solution would require overcoming the very strong hydrogen bonding in water, as well as the significantly strong dispersion forces between the relatively large oil molecules. And, since the polar water molecules and nonpolar oil molecules would not experience very strong intermolecular attraction, very little energy would be released by solvation.



A mixture of nonpolar cooking oil and polar water does not yield a solution. (credit: Gautam Dogra)

On the other hand, a mixture of ethanol and water will mix in any proportions to yield a solution. In this case, both substances are capable of hydrogen bonding, and so the solvation process is sufficiently exothermic to compensate for the endothermic separations of solute and solvent molecules.

As noted at the beginning of this module, spontaneous solution formation is favored, but not guaranteed, by exothermic dissolution processes. While

many soluble compounds do, indeed, dissolve with the release of heat, some dissolve endothermically. Ammonium nitrate (NH_4NO_3) is one such example and is used to make instant cold packs for treating injuries like the one pictured in [\[link\]](#). A thin-walled plastic bag of water is sealed inside a larger bag with solid NH_4NO_3 . When the smaller bag is broken, a solution of NH_4NO_3 forms, absorbing heat from the surroundings (the injured area to which the pack is applied) and providing a cold compress that decreases swelling. Endothermic dissolutions such as this one require a greater energy input to separate the solute species than is recovered when the solutes are solvated, but they are spontaneous nonetheless due to the increase in disorder that accompanies formation of the solution.



An instant cold pack gets cold when certain salts, such as ammonium

nitrate, dissolve in water—an endothermic process.

Note:



Watch this brief [video](#) illustrating endothermic and exothermic dissolution processes.

Key Concepts and Summary

A solution forms when two or more substances combine physically to yield a mixture that is homogeneous at the molecular level. The solvent is the most concentrated component and determines the physical state of the solution. The solutes are the other components typically present at concentrations less than that of the solvent. Solutions may form endothermically or exothermically, depending upon the relative magnitudes of solute and solvent intermolecular attractive forces. Ideal solutions form with no appreciable change in energy.

Chemistry End of Chapter Exercises

Exercise:

Problem:

How do solutions differ from compounds? From other mixtures?

Solution:

A solution can vary in composition, while a compound cannot vary in composition. Solutions are homogeneous at the molecular level, while other mixtures are heterogeneous.

Exercise:**Problem:**

Which of the principal characteristics of solutions can we see in the solutions of $\text{K}_2\text{Cr}_2\text{O}_7$ shown in [\[link\]](#)?

Exercise:**Problem:**

When KNO_3 is dissolved in water, the resulting solution is significantly colder than the water was originally.

- (a) Is the dissolution of KNO_3 an endothermic or an exothermic process?
 - (b) What conclusions can you draw about the intermolecular attractions involved in the process?
 - (c) Is the resulting solution an ideal solution?
-

Solution:

(a) The process is endothermic as the solution is consuming heat. (b) Attraction between the K^+ and NO_3^- ions is stronger than between the ions and water molecules (the ion-ion interactions have a lower, more negative energy). Therefore, the dissolution process increases the energy of the molecular interactions, and it consumes the thermal

energy of the solution to make up for the difference. (c) No, an ideal solution is formed with no appreciable heat release or consumption.

Exercise:

Problem: Give an example of each of the following types of solutions:

- (a) a gas in a liquid
- (b) a gas in a gas
- (c) a solid in a solid

Exercise:

Problem:

Indicate the most important types of intermolecular attractions in each of the following solutions:

- (a) The solution in [\[link\]](#).
 - (b) $\text{NO}(l)$ in $\text{CO}(l)$
 - (c) $\text{Cl}_2(g)$ in $\text{Br}_2(l)$
 - (d) $\text{HCl}(g)$ in benzene $\text{C}_6\text{H}_6(l)$
 - (e) Methanol $\text{CH}_3\text{OH}(l)$ in $\text{H}_2\text{O}(l)$
-

Solution:

- (a) ion-dipole forces; (b) dipole-dipole forces; (c) dispersion forces; (d) dispersion forces; (e) hydrogen bonding

Exercise:

Problem:

Predict whether each of the following substances would be more soluble in water (polar solvent) or in a hydrocarbon such as heptane (C_7H_{16} , nonpolar solvent):

- (a) vegetable oil (nonpolar)
- (b) isopropyl alcohol (polar)
- (c) potassium bromide (ionic)

Exercise:**Problem:**

Heat is released when some solutions form; heat is absorbed when other solutions form. Provide a molecular explanation for the difference between these two types of spontaneous processes.

Solution:

Heat is released when the total intermolecular forces (IMFs) between the solute and solvent molecules are stronger than the total IMFs in the pure solute and in the pure solvent: Breaking weaker IMFs and forming stronger IMFs releases heat. Heat is absorbed when the total IMFs in the solution are weaker than the total of those in the pure solute and in the pure solvent: Breaking stronger IMFs and forming weaker IMFs absorbs heat.

Exercise:**Problem:**

Solutions of hydrogen in palladium may be formed by exposing Pd metal to H_2 gas. The concentration of hydrogen in the palladium depends on the pressure of H_2 gas applied, but in a more complex fashion than can be described by Henry's law. Under certain conditions, 0.94 g of hydrogen gas is dissolved in 215 g of palladium metal (solution density = 10.8 g cm^3).

- (a) Determine the molarity of this solution.
- (b) Determine the molality of this solution.
- (c) Determine the percent by mass of hydrogen atoms in this solution.

Glossary

alloy

solid mixture of a metallic element and one or more additional elements

ideal solution

solution that forms with no accompanying energy change

solvation

exothermic process in which intermolecular attractive forces between the solute and solvent in a solution are established

spontaneous process

physical or chemical change that occurs without the addition of energy from an external source

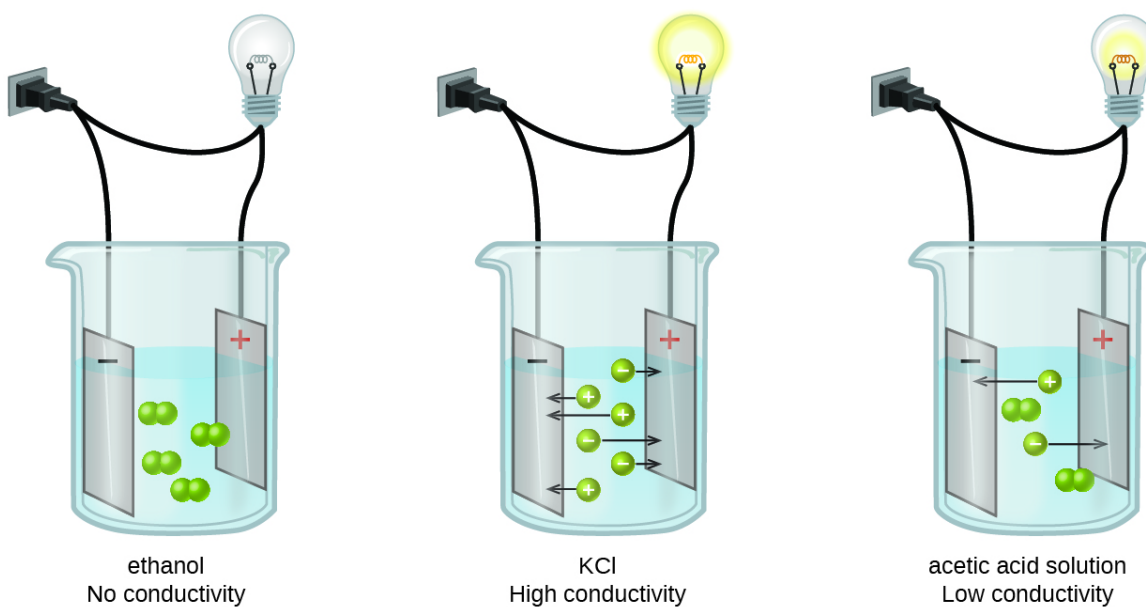
Electrolytes

By the end of this module, you will be able to:

- Define and give examples of electrolytes
- Distinguish between the physical and chemical changes that accompany dissolution of ionic and covalent electrolytes
- Relate electrolyte strength to solute-solvent attractive forces

When some substances are dissolved in water, they undergo either a physical or a chemical change that yields ions in solution. These substances constitute an important class of compounds called **electrolytes**. Substances that do not yield ions when dissolved are called **nonelectrolytes**. If the physical or chemical process that generates the ions is essentially 100% efficient (all of the dissolved compound yields ions), then the substance is known as a **strong electrolyte**. If only a relatively small fraction of the dissolved substance undergoes the ion-producing process, it is called a **weak electrolyte**.

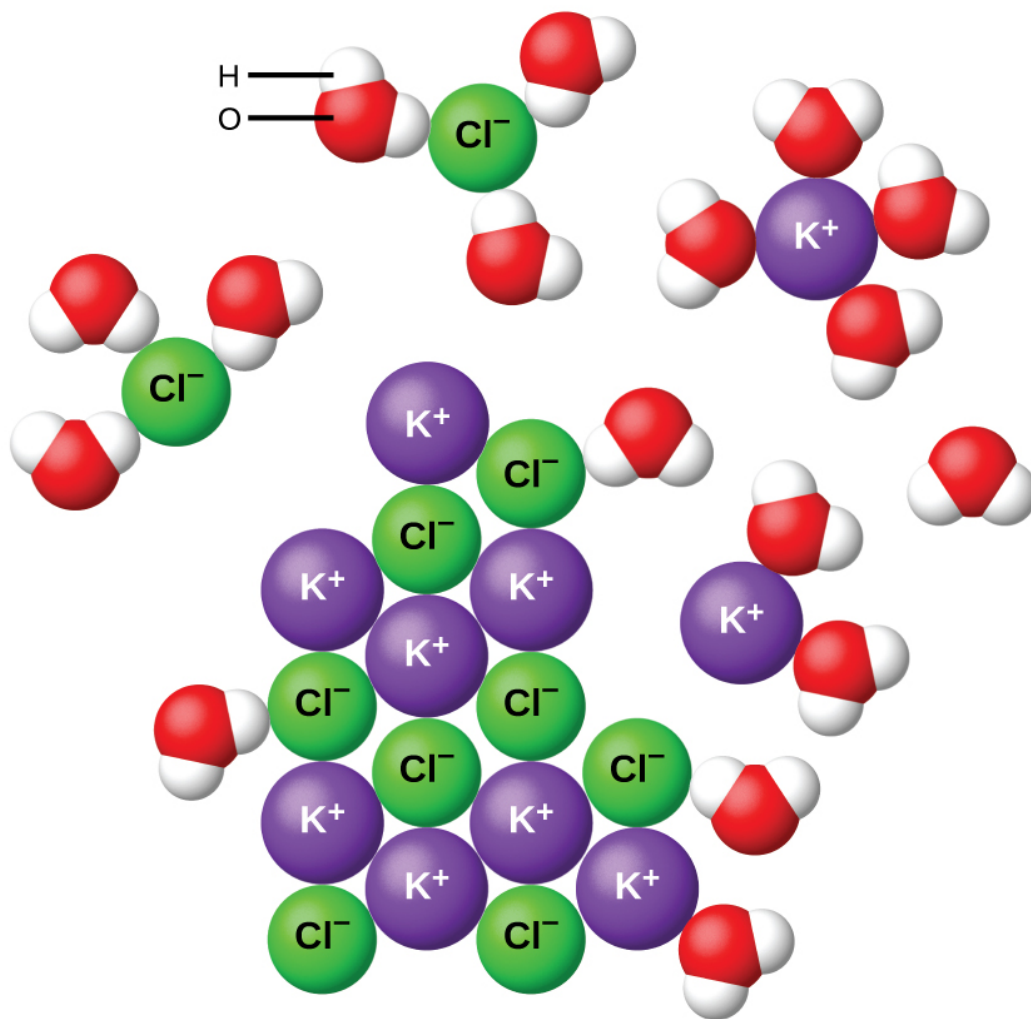
Substances may be identified as strong, weak, or nonelectrolytes by measuring the electrical conductance of an aqueous solution containing the substance. To conduct electricity, a substance must contain freely mobile, charged species. Most familiar is the conduction of electricity through metallic wires, in which case the mobile, charged entities are electrons. Solutions may also conduct electricity if they contain dissolved ions, with conductivity increasing as ion concentration increases. Applying a voltage to electrodes immersed in a solution permits assessment of the relative concentration of dissolved ions, either quantitatively, by measuring the electrical current flow, or qualitatively, by observing the brightness of a light bulb included in the circuit ([\[link\]](#)).



Solutions of nonelectrolytes such as ethanol do not contain dissolved ions and cannot conduct electricity. Solutions of electrolytes contain ions that permit the passage of electricity. The conductivity of an electrolyte solution is related to the strength of the electrolyte.

Ionic Electrolytes

Water and other polar molecules are attracted to ions, as shown in [\[link\]](#). The electrostatic attraction between an ion and a molecule with a dipole is called an **ion-dipole attraction**. These attractions play an important role in the dissolution of ionic compounds in water.



As potassium chloride (KCl) dissolves in water, the ions are hydrated. The polar water molecules are attracted by the charges on the K⁺ and Cl⁻ ions. Water molecules in front of and behind the ions are not shown.

When ionic compounds dissolve in water, the ions in the solid separate and disperse uniformly throughout the solution because water molecules surround and solvate the ions, reducing the strong electrostatic forces between them. This process represents a physical change known as **dissociation**. Under most conditions, ionic compounds will dissociate

nearly completely when dissolved, and so they are classified as strong electrolytes.

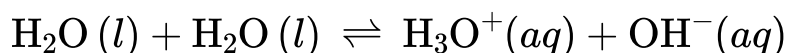
Let us consider what happens at the microscopic level when we add solid KCl to water. Ion-dipole forces attract the positive (hydrogen) end of the polar water molecules to the negative chloride ions at the surface of the solid, and they attract the negative (oxygen) ends to the positive potassium ions. The water molecules penetrate between individual K^+ and Cl^- ions and surround them, reducing the strong interionic forces that bind the ions together and letting them move off into solution as solvated ions, as [\[link\]](#) shows. The reduction of the electrostatic attraction permits the independent motion of each hydrated ion in a dilute solution, resulting in an increase in the disorder of the system as the ions change from their fixed and ordered positions in the crystal to mobile and much more disordered states in solution. This increased disorder is responsible for the dissolution of many ionic compounds, including KCl, which dissolve with absorption of heat.

In other cases, the electrostatic attractions between the ions in a crystal are so large, or the ion-dipole attractive forces between the ions and water molecules are so weak, that the increase in disorder cannot compensate for the energy required to separate the ions, and the crystal is insoluble. Such is the case for compounds such as calcium carbonate (limestone), calcium phosphate (the inorganic component of bone), and iron oxide (rust).

Covalent Electrolytes

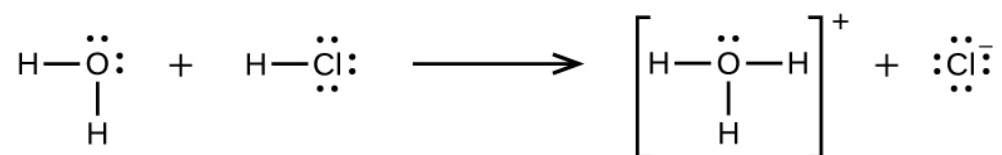
Pure water is an extremely poor conductor of electricity because it is only very slightly ionized—only about two out of every 1 billion molecules ionize at 25 °C. Water ionizes when one molecule of water gives up a proton (H^+ ion) to another molecule of water, yielding hydronium and hydroxide ions.

Equation:



In some cases, we find that solutions prepared from covalent compounds conduct electricity because the solute molecules react chemically with the solvent to produce ions. For example, pure hydrogen chloride is a gas consisting of covalent HCl molecules. This gas contains no ions. However, when we dissolve hydrogen chloride in water, we find that the solution is a very good conductor. The water molecules play an essential part in forming ions: Solutions of hydrogen chloride in many other solvents, such as benzene, do not conduct electricity and do not contain ions.

Hydrogen chloride is an *acid*, and so its molecules react with water, transferring H^+ ions to form hydronium ions (H_3O^+) and chloride ions (Cl^-):



This reaction is essentially 100% complete for HCl (i.e., it is a *strong acid* and, consequently, a strong electrolyte). Likewise, weak acids and bases that only react partially generate relatively low concentrations of ions when dissolved in water and are classified as weak electrolytes. The reader may wish to review the discussion of strong and weak acids provided in the earlier chapter of this text on reaction classes and stoichiometry.

Key Concepts and Summary

Substances that dissolve in water to yield ions are called electrolytes. Electrolytes may be covalent compounds that chemically react with water to produce ions (for example, acids and bases), or they may be ionic compounds that dissociate to yield their constituent cations and anions, when dissolved. Dissolution of an ionic compound is facilitated by ion-dipole attractions between the ions of the compound and the polar water molecules. Soluble ionic substances and strong acids ionize completely and are strong electrolytes, while weak acids and bases ionize to only a small extent and are weak electrolytes. Nonelectrolytes are substances that do not produce ions when dissolved in water.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Explain why the ions Na^+ and Cl^- are strongly solvated in water but not in hexane, a solvent composed of nonpolar molecules.

Solution:

Crystals of NaCl dissolve in water, a polar liquid with a very large dipole moment, and the individual ions become strongly solvated. Hexane is a nonpolar liquid with a dipole moment of zero and, therefore, does not significantly interact with the ions of the NaCl crystals.

Exercise:

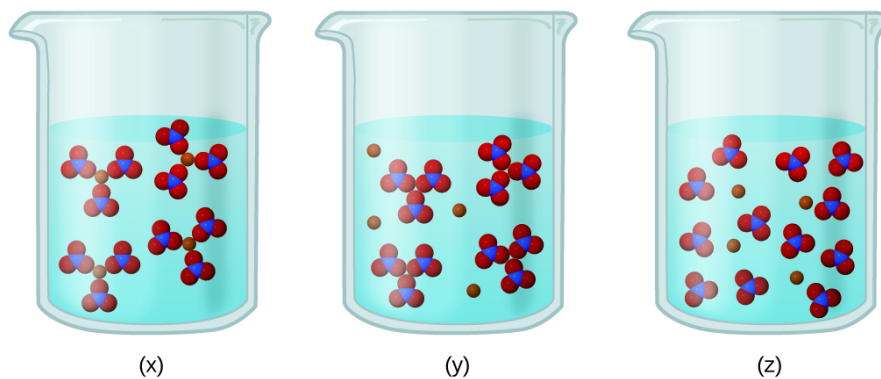
Problem:

Explain why solutions of HBr in benzene (a nonpolar solvent) are nonconductive, while solutions in water (a polar solvent) are conductive.

Exercise:

Problem: Consider the solutions presented:

(a) Which of the following sketches best represents the ions in a solution of $\text{Fe}(\text{NO}_3)_3(aq)$?



(b) Write a balanced chemical equation showing the products of the dissolution of $\text{Fe}(\text{NO}_3)_3$.

Solution:

(a) $\text{Fe}(\text{NO}_3)_3$ is a strong electrolyte, thus it should completely dissociate into Fe^{3+} and NO_3^- ions. Therefore, (z) best represents the solution. (b) $\text{Fe}(\text{NO}_3)_3(s) \longrightarrow \text{Fe}^{3+}(aq) + 3\text{NO}_3^-(aq)$

Exercise:

Problem:

Compare the processes that occur when methanol (CH_3OH), hydrogen chloride (HCl), and sodium hydroxide (NaOH) dissolve in water. Write equations and prepare sketches showing the form in which each of these compounds is present in its respective solution.

Exercise:

Problem:

What is the expected electrical conductivity of the following solutions?

- (a) $\text{NaOH}(aq)$
- (b) $\text{HCl}(aq)$
- (c) $\text{C}_6\text{H}_{12}\text{O}_6(aq)$ (glucose)
- (d) $\text{NH}_3(aq)$

Solution:

(a) high conductivity (solute is an ionic compound that will dissociate when dissolved); (b) high conductivity (solute is a strong acid and will ionize completely when dissolved); (c) nonconductive (solute is a covalent compound, neither acid nor base, unreactive towards water); (d) low conductivity (solute is a weak base and will partially ionize when dissolved)

Exercise:**Problem:**

Why are most *solid* ionic compounds electrically nonconductive, whereas aqueous solutions of ionic compounds are good conductors? Would you expect a *liquid* (molten) ionic compound to be electrically conductive or nonconductive? Explain.

Exercise:**Problem:**

Indicate the most important type of intermolecular attraction responsible for solvation in each of the following solutions:

- (a) the solutions in [\[link\]](#)
- (b) methanol, CH_3OH , dissolved in ethanol, $\text{C}_2\text{H}_5\text{OH}$
- (c) methane, CH_4 , dissolved in benzene, C_6H_6
- (d) the polar halocarbon CF_2Cl_2 dissolved in the polar halocarbon $\text{CF}_2\text{ClCFCl}_2$
- (e) $\text{O}_2(l)$ in $\text{N}_2(l)$

Solution:

(a) ion-dipole; (b) hydrogen bonds; (c) dispersion forces; (d) dipole-dipole attractions; (e) dispersion forces

Glossary

dissociation

physical process accompanying the dissolution of an ionic compound in which the compound's constituent ions are solvated and dispersed throughout the solution

electrolyte

substance that produces ions when dissolved in water

ion-dipole attraction

electrostatic attraction between an ion and a polar molecule

nonelectrolyte

substance that does not produce ions when dissolved in water

strong electrolyte

substance that dissociates or ionizes completely when dissolved in water

weak electrolyte

substance that ionizes only partially when dissolved in water

Solubility

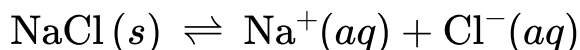
By the end of this module, you will be able to:

- Describe the effects of temperature and pressure on solubility
- State Henry's law and use it in calculations involving the solubility of a gas in a liquid
- Explain the degrees of solubility possible for liquid-liquid solutions

Imagine adding a small amount of salt to a glass of water, stirring until all the salt has dissolved, and then adding a bit more. You can repeat this process until the salt concentration of the solution reaches its natural limit, a limit determined primarily by the relative strengths of the solute-solute, solute-solvent, and solvent-solvent attractive forces discussed in the previous two modules of this chapter. You can be certain that you have reached this limit because, no matter how long you stir the solution, undissolved salt remains. The concentration of salt in the solution at this point is known as its solubility.

The **solubility** of a solute in a particular solvent is the maximum concentration that may be achieved under given conditions when the dissolution process is *at equilibrium*. Referring to the example of salt in water:

Equation:



When a solute's concentration is equal to its solubility, the solution is said to be **saturated** with that solute. If the solute's concentration is less than its solubility, the solution is said to be **unsaturated**. A solution that contains a relatively low concentration of solute is called dilute, and one with a relatively high concentration is called concentrated.

If we add more salt to a saturated solution of salt, we see it fall to the bottom and no more seems to dissolve. In fact, the added salt does dissolve, as represented by the forward direction of the dissolution equation. Accompanying this process, dissolved salt will precipitate, as depicted by the reverse direction of the equation. The system is said to be at equilibrium

when these two reciprocal processes are occurring at equal rates, and so the amount of undissolved and dissolved salt remains constant. Support for the simultaneous occurrence of the dissolution and precipitation processes is provided by noting that the number and sizes of the undissolved salt crystals will change over time, though their combined mass will remain the same.

Note:



Use this [interactive simulation](#) to prepare various saturated solutions.

Solutions may be prepared in which a solute concentration *exceeds* its solubility. Such solutions are said to be **supersaturated**, and they are interesting examples of *nonequilibrium* states. For example, the carbonated beverage in an open container that has not yet “gone flat” is supersaturated with carbon dioxide gas; given time, the CO_2 concentration will decrease until it reaches its equilibrium value.

Note:

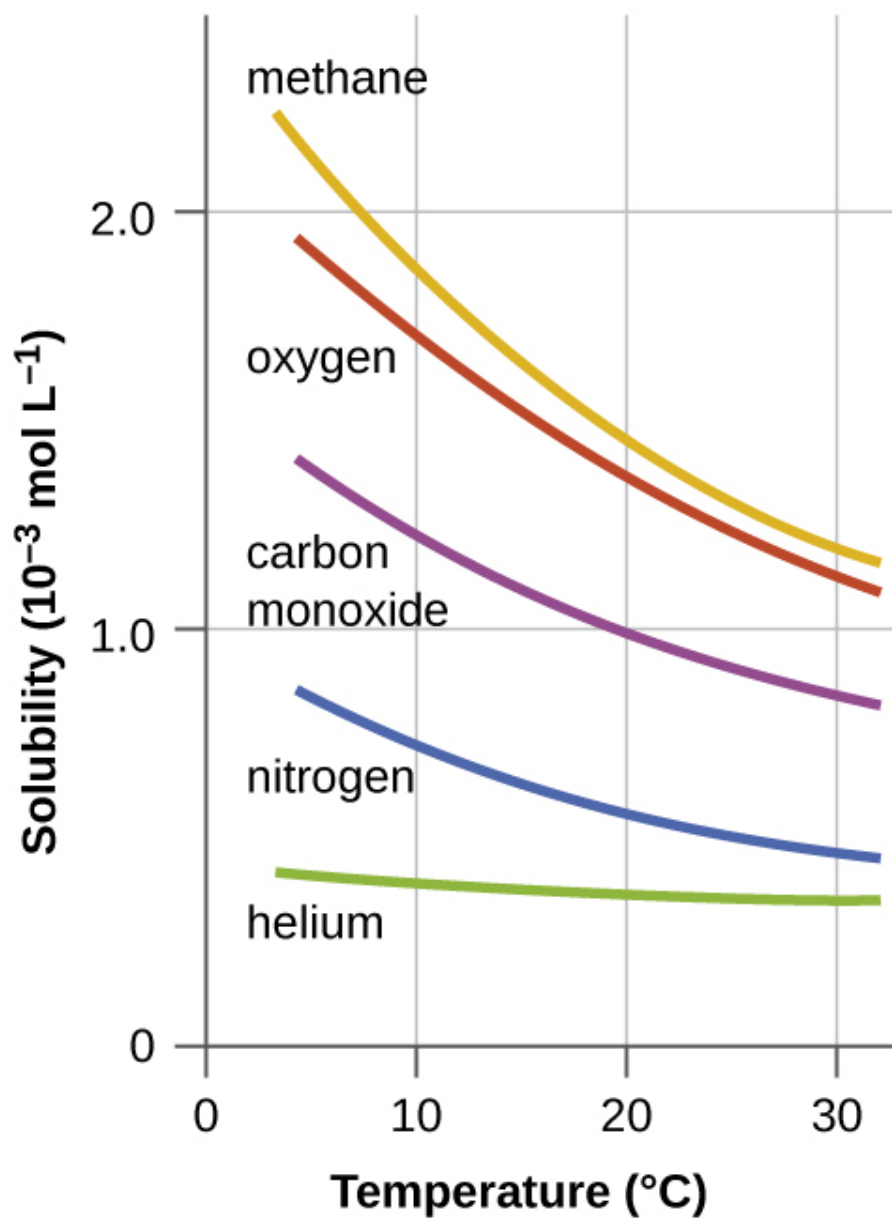


Watch this [impressive video](#) showing the precipitation of sodium acetate from a supersaturated solution.

Solutions of Gases in Liquids

In an earlier module of this chapter, the effect of intermolecular attractive forces on solution formation was discussed. The chemical structures of the solute and solvent dictate the types of forces possible and, consequently, are important factors in determining solubility. For example, under similar conditions, the water solubility of oxygen is approximately three times greater than that of helium, but 100 times less than the solubility of chloromethane, CHCl_3 . Considering the role of the solvent's chemical structure, note that the solubility of oxygen in the liquid hydrocarbon hexane, C_6H_{14} , is approximately 20 times greater than it is in water.

Other factors also affect the solubility of a given substance in a given solvent. Temperature is one such factor, with gas solubility typically decreasing as temperature increases ([link](#)). This is one of the major impacts resulting from the thermal pollution of natural bodies of water.



The solubilities of these gases in water decrease as the temperature increases. All solubilities were measured with a constant pressure of 101.3 kPa (1 atm) of gas above the solutions.

When the temperature of a river, lake, or stream is raised abnormally high, usually due to the discharge of hot water from some industrial process, the

solubility of oxygen in the water is decreased. Decreased levels of dissolved oxygen may have serious consequences for the health of the water's ecosystems and, in severe cases, can result in large-scale fish kills ([link](#)).



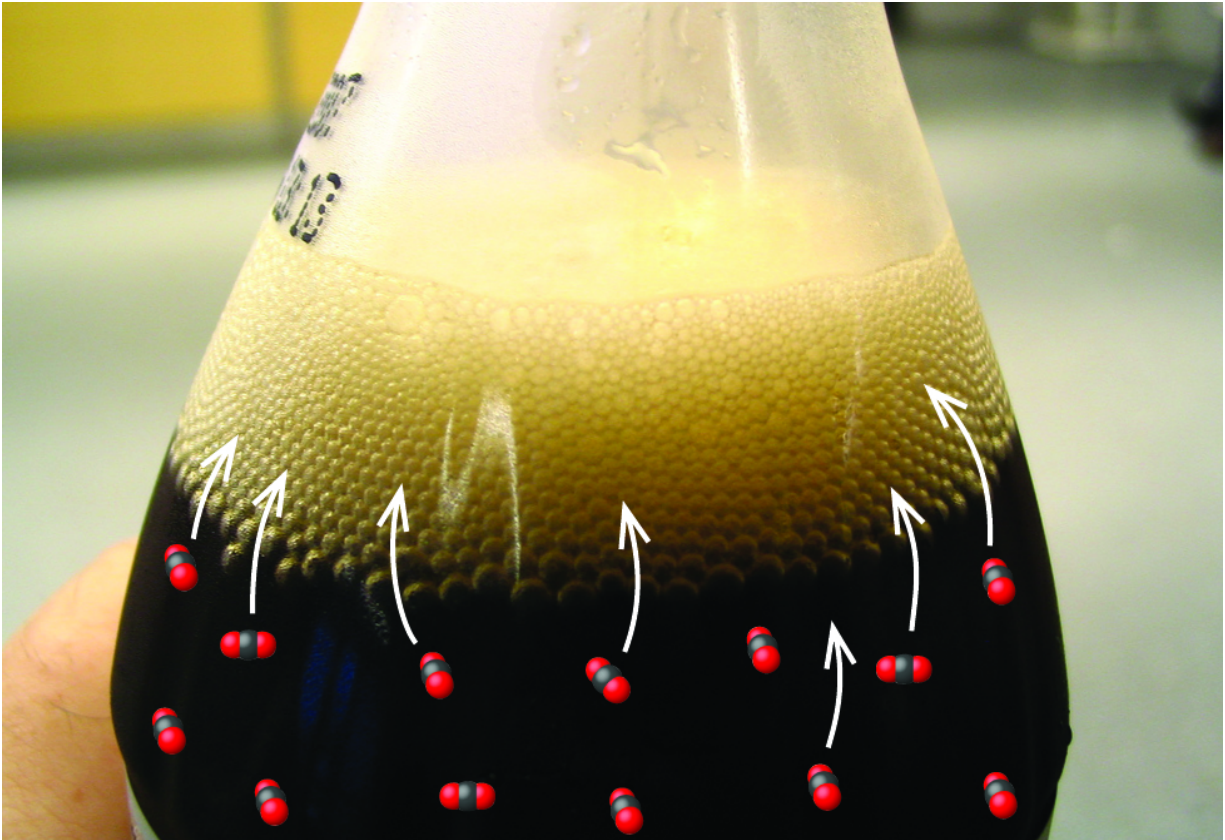
(a)



(b)

(a) The small bubbles of air in this glass of chilled water formed when the water warmed to room temperature and the solubility of its dissolved air decreased. (b) The decreased solubility of oxygen in natural waters subjected to thermal pollution can result in large-scale fish kills. (credit a: modification of work by Liz West; credit b: modification of work by U.S. Fish and Wildlife Service)

The solubility of a gaseous solute is also affected by the partial pressure of solute in the gas to which the solution is exposed. Gas solubility increases as the pressure of the gas increases. Carbonated beverages provide a nice illustration of this relationship. The carbonation process involves exposing the beverage to a relatively high pressure of carbon dioxide gas and then sealing the beverage container, thus saturating the beverage with CO_2 at this pressure. When the beverage container is opened, a familiar hiss is heard as the carbon dioxide gas pressure is released, and some of the dissolved carbon dioxide is typically seen leaving solution in the form of small bubbles ([link](#)). At this point, the beverage is *supersaturated* with carbon dioxide and, with time, the dissolved carbon dioxide concentration will decrease to its equilibrium value and the beverage will become “flat.”



Opening the bottle of carbonated beverage reduces the pressure of the *gaseous* carbon dioxide above the beverage. The solubility of CO_2 is thus lowered, and some *dissolved* carbon dioxide may be seen leaving the solution as small gas bubbles. (credit: modification of work by Derrick Coetzee)

For many gaseous solutes, the relation between solubility, C_g , and partial pressure, P_g , is a proportional one:

Equation:

$$C_g = kP_g$$

where k is a proportionality constant that depends on the identities of the gaseous solute and solvent, and on the solution temperature. This is a mathematical statement of **Henry's law**: *The quantity of an ideal gas that*

dissolves in a definite volume of liquid is directly proportional to the pressure of the gas.

Example:

Application of Henry's Law

At 20 °C, the concentration of dissolved oxygen in water exposed to gaseous oxygen at a partial pressure of 101.3 kPa (760 torr) is $1.38 \times 10^{-3} \text{ mol L}^{-1}$. Use Henry's law to determine the solubility of oxygen when its partial pressure is 20.7 kPa (155 torr), the approximate pressure of oxygen in earth's atmosphere.

Solution

According to Henry's law, for an ideal solution the solubility, C_g , of a gas ($1.38 \times 10^{-3} \text{ mol L}^{-1}$, in this case) is directly proportional to the pressure, P_g , of the undissolved gas above the solution (101.3 kPa, or 760 torr, in this case). Because we know both C_g and P_g , we can rearrange this expression to solve for k .

Equation:

$$\begin{aligned}C_g &= kP_g \\k &= \frac{C_g}{P_g} \\&= \frac{1.38 \times 10^{-3} \text{ mol L}^{-1}}{101.3 \text{ kPa}} \\&= 1.36 \times 10^{-5} \text{ mol L}^{-1} \text{ kPa}^{-1} \\&\quad (1.82 \times 10^{-6} \text{ mol L}^{-1} \text{ torr}^{-1})\end{aligned}$$

Now we can use k to find the solubility at the lower pressure.

Equation:

$$C_g = kP_g$$

Equation:

$$\begin{aligned}
 &1.36 \times 10^{-5} \text{ mol L}^{-1} \text{ kPa}^{-1} \times 20.7 \text{ kPa} \\
 &(\text{or } 1.82 \times 10^{-6} \text{ mol L}^{-1} \text{ torr}^{-1} \times 155 \text{ torr}) \\
 &= 2.82 \times 10^{-4} \text{ mol L}^{-1}
 \end{aligned}$$

Note that various units may be used to express the quantities involved in these sorts of computations. Any combination of units that yield to the constraints of dimensional analysis are acceptable.

Check Your Learning

Exposing a 100.0 mL sample of water at 0 °C to an atmosphere containing a gaseous solute at 20.26 kPa (152 torr) resulted in the dissolution of 1.45×10^{-3} g of the solute. Use Henry's law to determine the solubility of this gaseous solute when its pressure is 101.3 kPa (760 torr).

Note:

Answer:

7.25×10^{-3} in 100.0 mL or 0.0725 g/L

Note:

Decompression Sickness or “The Bends”

Decompression sickness (DCS), or “the bends,” is an effect of the increased pressure of the air inhaled by scuba divers when swimming underwater at considerable depths. In addition to the pressure exerted by the atmosphere, divers are subjected to additional pressure due to the water above them, experiencing an increase of approximately 1 atm for each 10 m of depth. Therefore, the air inhaled by a diver while submerged contains gases at the corresponding higher ambient pressure, and the concentrations of the gases dissolved in the diver's blood are proportionally higher per Henry's law.

As the diver ascends to the surface of the water, the ambient pressure decreases and the dissolved gases become less soluble. If the ascent is too

rapid, the gases escaping from the diver's blood may form bubbles that can cause a variety of symptoms ranging from rashes and joint pain to paralysis and death. To avoid DCS, divers must ascend from depths at relatively slow speeds (10 or 20 m/min) or otherwise make several decompression stops, pausing for several minutes at given depths during the ascent. When these preventive measures are unsuccessful, divers with DCS are often provided hyperbaric oxygen therapy in pressurized vessels called decompression (or recompression) chambers ([\[link\]](#)).



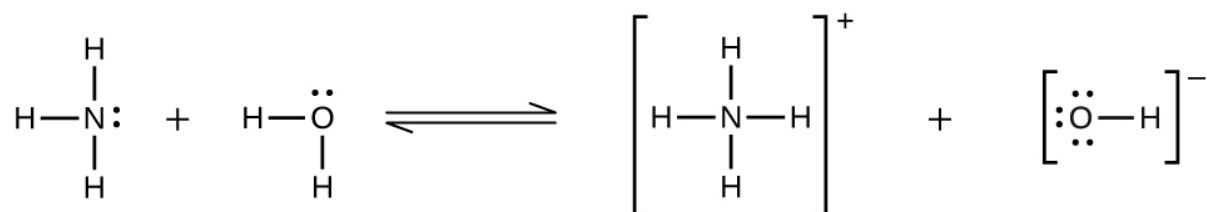
(a)



(b)

(a) US Navy divers undergo training in a recompression chamber. (b) Divers receive hyperbaric oxygen therapy.

Deviations from Henry's law are observed when a chemical reaction takes place between the gaseous solute and the solvent. Thus, for example, the solubility of ammonia in water does not increase as rapidly with increasing pressure as predicted by the law because ammonia, being a base, reacts to some extent with water to form ammonium ions and hydroxide ions.



Gases can form supersaturated solutions. If a solution of a gas in a liquid is prepared either at low temperature or under pressure (or both), then as the solution warms or as the gas pressure is reduced, the solution may become supersaturated. In 1986, more than 1700 people in Cameroon were killed when a cloud of gas, almost certainly carbon dioxide, bubbled from Lake Nyos ([link](#)), a deep lake in a volcanic crater. The water at the bottom of Lake Nyos is saturated with carbon dioxide by volcanic activity beneath the lake. It is believed that the lake underwent a turnover due to gradual heating from below the lake, and the warmer, less-dense water saturated with carbon dioxide reached the surface. Consequently, tremendous quantities of dissolved CO_2 were released, and the colorless gas, which is denser than air, flowed down the valley below the lake and suffocated humans and animals living in the valley.



(a)



(b)

(a) It is believed that the 1986 disaster that killed more than 1700 people near Lake Nyos in Cameroon resulted when a large volume of carbon dioxide gas was released from the lake. (b) A CO_2 vent has since been installed to help outgas the lake in a slow, controlled fashion and prevent a similar catastrophe from happening in the future.

(credit a: modification of work by Jack Lockwood; credit b:
modification of work by Bill Evans)

Solutions of Liquids in Liquids

We know that some liquids mix with each other in all proportions; in other words, they have infinite mutual solubility and are said to be **miscible**.

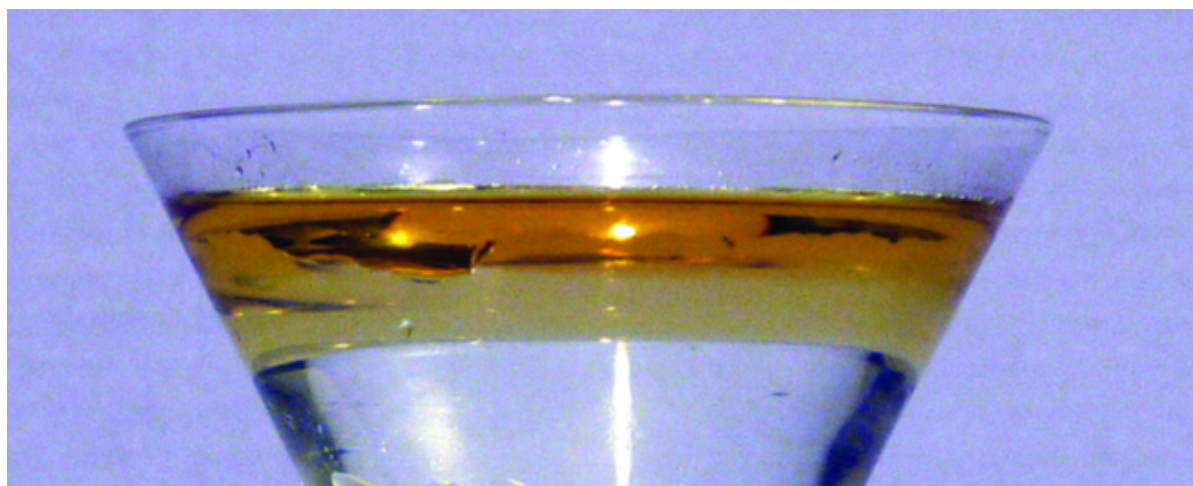
Ethanol, sulfuric acid, and ethylene glycol (popular for use as antifreeze, pictured in [\[link\]](#)) are examples of liquids that are completely miscible with water. Two-cycle motor oil is miscible with gasoline.



Water and antifreeze are miscible; mixtures of the two are homogeneous in all proportions. (credit: “dno1967”/Wikimedia commons)

Liquids that mix with water in all proportions are usually polar substances or substances that form hydrogen bonds. For such liquids, the dipole-dipole attractions (or hydrogen bonding) of the solute molecules with the solvent molecules are at least as strong as those between molecules in the pure solute or in the pure solvent. Hence, the two kinds of molecules mix easily. Likewise, nonpolar liquids are miscible with each other because there is no appreciable difference in the strengths of solute-solute, solvent-solvent, and solute-solvent intermolecular attractions. The solubility of polar molecules in polar solvents and of nonpolar molecules in nonpolar solvents is, again, an illustration of the chemical axiom “like dissolves like.”

Two liquids that do not mix to an appreciable extent are called **immiscible**. Layers are formed when we pour immiscible liquids into the same container. Gasoline, oil ([\[link\]](#)), benzene, carbon tetrachloride, some paints, and many other nonpolar liquids are immiscible with water. The attraction between the molecules of such nonpolar liquids and polar water molecules is ineffectively weak. The only strong attractions in such a mixture are between the water molecules, so they effectively squeeze out the molecules of the nonpolar liquid. The distinction between immiscibility and miscibility is really one of degrees, so that miscible liquids are of infinite mutual solubility, while liquids said to be immiscible are of very low (though not zero) mutual solubility.





Water and oil are immiscible. Mixtures of these two substances will form two separate layers with the less dense oil floating on top of the water. (credit: “Yortw”/Flickr)

Two liquids, such as bromine and water, that are of *moderate* mutual solubility are said to be **partially miscible**. Two partially miscible liquids usually form two layers when mixed. In the case of the bromine and water

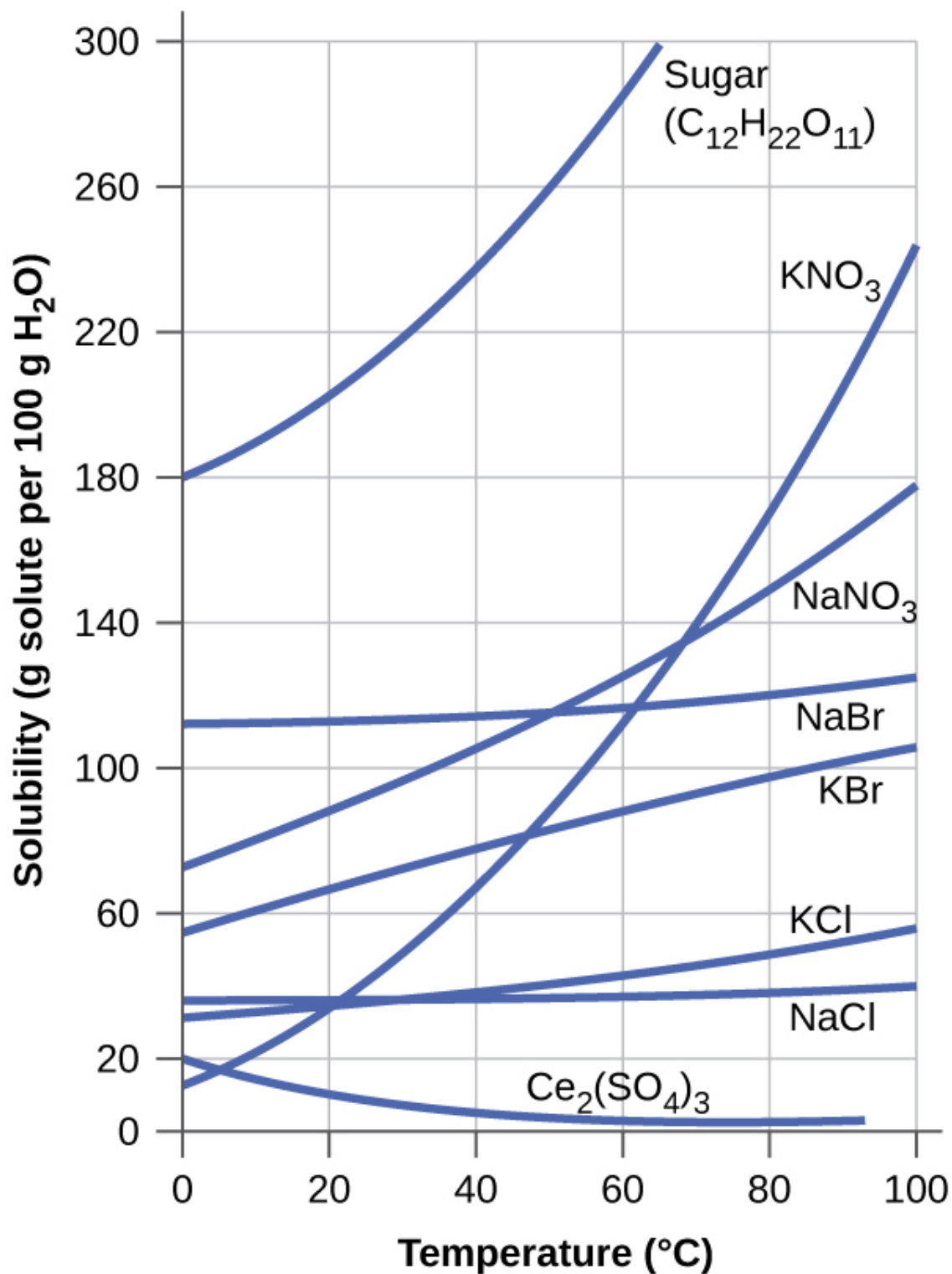
mixture, the upper layer is water, saturated with bromine, and the lower layer is bromine saturated with water. Since bromine is nonpolar, and, thus, not very soluble in water, the water layer is only slightly discolored by the bright orange bromine dissolved in it. Since the solubility of water in bromine is very low, there is no noticeable effect on the dark color of the bromine layer ([link](#)).



Bromine (the deep orange liquid on the left) and water (the clear liquid in the middle) are partially miscible. The top layer in the mixture on the right is a saturated solution of bromine in water; the bottom layer is a saturated solution of water in bromine. (credit: Paul Flowers)

Solutions of Solids in Liquids

The dependence of solubility on temperature for a number of solids in water is shown by the solubility curves in [\[link\]](#). Reviewing these data indicate a general trend of increasing solubility with temperature, although there are exceptions, as illustrated by the ionic compound cerium sulfate.



This graph shows how the solubility of several solids changes with temperature.

The temperature dependence of solubility can be exploited to prepare supersaturated solutions of certain compounds. A solution may be saturated with the compound at an elevated temperature (where the solute is more soluble) and subsequently cooled to a lower temperature without precipitating the solute. The resultant solution contains solute at a concentration greater than its equilibrium solubility at the lower temperature (i.e., it is supersaturated) and is relatively stable. Precipitation of the excess solute can be initiated by adding a seed crystal (see the video in the Link to Learning earlier in this module) or by mechanically agitating the solution. Some hand warmers, such as the one pictured in [\[link\]](#), take advantage of this behavior.



This hand warmer produces heat when the sodium acetate in a supersaturated solution precipitates. Precipitation of the solute is initiated by a mechanical shockwave generated when the flexible metal disk within the solution is “clicked.” (credit: modification of work by “Velela”/Wikimedia Commons)

Note:



This [video](#) shows the crystallization process occurring in a hand warmer.

Key Concepts and Summary

The extent to which one substance will dissolve in another is determined by several factors, including the types and relative strengths of intermolecular attractive forces that may exist between the substances' atoms, ions, or molecules. This tendency to dissolve is quantified as a substance's solubility, its maximum concentration in a solution at equilibrium under specified conditions. A saturated solution contains solute at a concentration equal to its solubility. A supersaturated solution is one in which a solute's concentration exceeds its solubility—a nonequilibrium (unstable) condition that will result in solute precipitation when the solution is appropriately perturbed. Miscible liquids are soluble in all proportions, and immiscible liquids exhibit very low mutual solubility. Solubilities for gaseous solutes decrease with increasing temperature, while those for most, but not all, solid solutes increase with temperature. The concentration of a gaseous solute in a solution is proportional to the partial pressure of the gas to which the solution is exposed, a relation known as Henry's law.

Key Equations

- $C_g = kP_g$

Chemistry End of Chapter Exercises

Exercise:

Problem:

Suppose you are presented with a clear solution of sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$. How could you determine whether the solution is unsaturated, saturated, or supersaturated?

Exercise:**Problem:**

Supersaturated solutions of most solids in water are prepared by cooling saturated solutions. Supersaturated solutions of most gases in water are prepared by heating saturated solutions. Explain the reasons for the difference in the two procedures.

Solution:

The solubility of solids usually decreases upon cooling a solution, while the solubility of gases usually decreases upon heating.

Exercise:**Problem:**

Suggest an explanation for the observations that ethanol, $\text{C}_2\text{H}_5\text{OH}$, is completely miscible with water and that ethanethiol, $\text{C}_2\text{H}_5\text{SH}$, is soluble only to the extent of 1.5 g per 100 mL of water.

Exercise:**Problem:**

Calculate the percent by mass of KBr in a saturated solution of KBr in water at 10 °C. See [\[link\]](#) for useful data, and report the computed percentage to one significant digit.

Solution:

40%

Exercise:

Problem:

Which of the following gases is expected to be most soluble in water? Explain your reasoning.

- (a) CH_4
- (b) CCl_4
- (c) CHCl_3

Exercise:**Problem:**

At 0 °C and 1.00 atm, as much as 0.70 g of O_2 can dissolve in 1 L of water. At 0 °C and 4.00 atm, how many grams of O_2 dissolve in 1 L of water?

Solution:

2.8 g

Exercise:

Problem: Refer to [\[link\]](#).

- (a) How did the concentration of dissolved CO_2 in the beverage change when the bottle was opened?
- (b) What caused this change?
- (c) Is the beverage unsaturated, saturated, or supersaturated with CO_2 ?

Exercise:

Problem:

The Henry's law constant for CO_2 is $3.4 \times 10^{-2} \text{ M/atm}$ at 25°C . What pressure of carbon dioxide is needed to maintain a CO_2 concentration of 0.10 M in a can of lemon-lime soda?

Solution:

2.9 atm

Exercise:**Problem:**

The Henry's law constant for O_2 is $1.3 \times 10^{-3} \text{ M/atm}$ at 25°C . What mass of oxygen would be dissolved in a 40-L aquarium at 25°C , assuming an atmospheric pressure of 1.00 atm, and that the partial pressure of O_2 is 0.21 atm?

Exercise:**Problem:**

How many liters of HCl gas, measured at 30.0°C and 745 torr, are required to prepare 1.25 L of a 3.20-M solution of hydrochloric acid?

Solution:

102 L HCl

Glossary**Henry's law**

law stating the proportional relationship between the concentration of dissolved gas in a solution and the partial pressure of the gas in contact with the solution

immiscible

of negligible mutual solubility; typically refers to liquid substances

miscible

mutually soluble in all proportions; typically refers to liquid substances

partially miscible

of moderate mutual solubility; typically refers to liquid substances

saturated

of concentration equal to solubility; containing the maximum concentration of solute possible for a given temperature and pressure

solubility

extent to which a solute may be dissolved in water, or any solvent

supersaturated

of concentration that exceeds solubility; a nonequilibrium state

unsaturated

of concentration less than solubility

Colligative Properties

By the end of this section, you will be able to:

- Express concentrations of solution components using mole fraction and molality
- Describe the effect of solute concentration on various solution properties (vapor pressure, boiling point, freezing point, and osmotic pressure)
- Perform calculations using the mathematical equations that describe these various colligative effects
- Describe the process of distillation and its practical applications
- Explain the process of osmosis and describe how it is applied industrially and in nature

The properties of a solution are different from those of either the pure solute(s) or solvent. Many solution properties are dependent upon the chemical identity of the solute. Compared to pure water, a solution of hydrogen chloride is more acidic, a solution of ammonia is more basic, a solution of sodium chloride is more dense, and a solution of sucrose is more viscous. There are a few solution properties, however, that depend *only* upon the total concentration of solute species, regardless of their identities. These **colligative properties** include vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure. This small set of properties is of central importance to many natural phenomena and technological applications, as will be described in this module.

Mole Fraction and Molality

Several units commonly used to express the concentrations of solution components were introduced in an earlier chapter of this text, each providing certain benefits for use in different applications. For example, molarity (M) is a convenient unit for use in stoichiometric calculations, since it is defined in terms of the molar amounts of solute species:

Equation:

$$M = \frac{\text{mol solute}}{\text{L solution}}$$

Because solution volumes vary with temperature, molar concentrations will likewise vary. When expressed as molarity, the concentration of a solution with identical numbers of solute and solvent species will be different at different temperatures, due to the contraction/expansion of the solution. More appropriate for calculations involving many colligative properties are mole-based concentration units whose values are not dependent on temperature. Two such units are *mole fraction* (introduced in the previous chapter on gases) and *molality*.

The mole fraction, X , of a component is the ratio of its molar amount to the total number of moles of all solution components:

Equation:

$$X_A = \frac{\text{mol A}}{\text{total mol of all components}}$$

Molality is a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms:

Equation:

$$m = \frac{\text{mol solute}}{\text{kg solvent}}$$

Since these units are computed using only masses and molar amounts, they do not vary with temperature and, thus, are better suited for applications requiring temperature-independent concentrations, including several colligative properties, as will be described in this chapter module.

Example:

Calculating Mole Fraction and Molality

The antifreeze in most automobile radiators is a mixture of equal volumes of ethylene glycol and water, with minor amounts of other additives that prevent corrosion. What are the (a) mole fraction and (b) molality of ethylene glycol, $\text{C}_2\text{H}_4(\text{OH})_2$, in a solution prepared from 2.22×10^3 g of ethylene glycol and 2.00×10^3 g of water (approximately 2 L of glycol and 2 L of water)?

Solution

(a) The mole fraction of ethylene glycol may be computed by first deriving molar amounts of both solution components and then substituting these amounts into the unit definition.

Equation:

$$\begin{aligned}\text{mol C}_2\text{H}_4(\text{OH})_2 &= 2.22 \times 10^3 \text{ g} \times \frac{1 \text{ mol C}_2\text{H}_4(\text{OH})_2}{62.07 \text{ g C}_2\text{H}_4(\text{OH})_2} = 35.8 \text{ mol C}_2\text{H}_4(\text{OH})_2 \\ \text{mol H}_2\text{O} &= 2.00 \times 10^3 \text{ g} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 111 \text{ mol H}_2\text{O} \\ X_{\text{ethylene glycol}} &= \frac{35.8 \text{ mol C}_2\text{H}_4(\text{OH})_2}{(35.8 + 111) \text{ mol total}} = 0.244\end{aligned}$$

Notice that mole fraction is a dimensionless property, being the ratio of properties with identical units (moles).

(b) To find molality, we need to know the moles of the solute and the mass of the solvent (in kg). First, use the given mass of ethylene glycol and its molar mass to find the moles of solute:

Equation:

$$2.22 \times 10^3 \text{ g C}_2\text{H}_4(\text{OH})_2 \left(\frac{1 \text{ mol C}_2\text{H}_4(\text{OH})_2}{62.07 \text{ g}} \right) = 35.8 \text{ mol C}_2\text{H}_4(\text{OH})_2$$

Then, convert the mass of the water from grams to kilograms:

Equation:

$$2.00 \times 10^3 \text{ g H}_2\text{O} \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) = 2.00 \text{ kg H}_2\text{O}$$

Finally, calculate molality per its definition:

Equation:

$$\begin{aligned}\text{molality} &= \frac{\text{mol solute}}{\text{kg solvent}} \\ \text{molality} &= \frac{35.8 \text{ mol C}_2\text{H}_4(\text{OH})_2}{2 \text{ kg H}_2\text{O}} \\ \text{molality} &= 17.9 \text{ m}\end{aligned}$$

Check Your Learning

What are the mole fraction and molality of a solution that contains 0.850 g of ammonia, NH_3 , dissolved in 125 g of water?

Note:

Answer:

7.14×10^{-3} ; 0.399 *m*

Example:**Converting Mole Fraction and Molal Concentrations**

Calculate the mole fraction of solute and solvent in a 3.0 *m* solution of sodium chloride.

Solution

Converting from one concentration unit to another is accomplished by first comparing the two unit definitions. In this case, both units have the same numerator (moles of solute) but different denominators. The provided molal concentration may be written as:

Equation:

$$\frac{3.0 \text{ mol NaCl}}{1.0 \text{ kg H}_2\text{O}}$$

The numerator for this solution's mole fraction is, therefore, 3.0 mol NaCl. The denominator may be computed by deriving the molar amount of water corresponding to 1.0 kg

Equation:

$$1.0 \text{ kg H}_2\text{O} \left(\frac{1000 \text{ g}}{1 \text{ kg}} \right) \left(\frac{\text{mol H}_2\text{O}}{18.02 \text{ g}} \right) = 55 \text{ mol H}_2\text{O}$$

and then substituting these molar amounts into the definition for mole fraction.

Equation:

$$\begin{aligned} X_{\text{H}_2\text{O}} &= \frac{\text{mol H}_2\text{O}}{\text{mol NaCl} + \text{mol H}_2\text{O}} \\ X_{\text{H}_2\text{O}} &= \frac{55 \text{ mol H}_2\text{O}}{3.0 \text{ mol NaCl} + 55 \text{ mol H}_2\text{O}} \\ X_{\text{H}_2\text{O}} &= 0.95 \\ X_{\text{NaCl}} &= \frac{\text{mol NaCl}}{\text{mol NaCl} + \text{mol H}_2\text{O}} \\ X_{\text{NaCl}} &= \frac{3.0 \text{ mol NaCl}}{3.0 \text{ mol NaCl} + 55 \text{ mol H}_2\text{O}} \\ X_{\text{NaCl}} &= 0.052 \end{aligned}$$

Check Your Learning

The mole fraction of iodine, I_2 , dissolved in dichloromethane, CH_2Cl_2 , is 0.115. What is the molal concentration, *m*, of iodine in this solution?

Note:

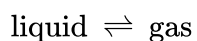
Answer:

1.50 m

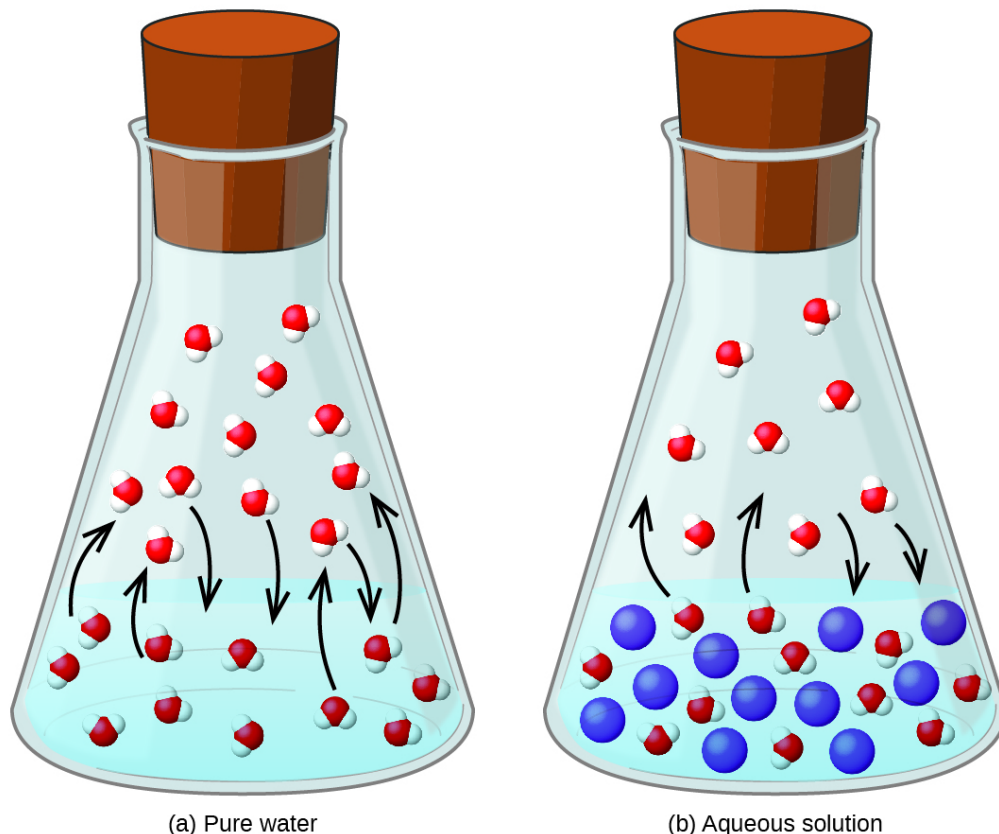
Vapor Pressure Lowering

As described in the chapter on liquids and solids, the equilibrium vapor pressure of a liquid is the pressure exerted by its gaseous phase when vaporization and condensation are occurring at equal rates:

Equation:



Dissolving a nonvolatile substance in a volatile liquid results in a lowering of the liquid's vapor pressure. This phenomenon can be rationalized by considering the effect of added solute molecules on the liquid's vaporization and condensation processes. To vaporize, solvent molecules must be present at the surface of the solution. The presence of solute decreases the surface area available to solvent molecules and thereby reduces the rate of solvent vaporization. Since the rate of condensation is unaffected by the presence of solute, the net result is that the vaporization-condensation equilibrium is achieved with fewer solvent molecules in the vapor phase (i.e., at a lower vapor pressure) ([link](#)). While this kinetic interpretation is useful, it does not account for several important aspects of the colligative nature of vapor pressure lowering. A more rigorous explanation involves the property of *entropy*, a topic of discussion in a later text chapter on thermodynamics. For purposes of understanding the lowering of a liquid's vapor pressure, it is adequate to note that the greater entropy of a solution in comparison to its separate solvent and solute serves to effectively stabilize the solvent molecules and hinder their vaporization. A lower vapor pressure results, and a correspondingly higher boiling point as described in the next section of this module.



The presence of nonvolatile solutes lowers the vapor pressure of a solution by impeding the evaporation of solvent molecules.

The relationship between the vapor pressures of solution components and the concentrations of those components is described by **Raoult's law**: *The partial pressure exerted by any component of an ideal solution is equal to the vapor pressure of the pure component multiplied by its mole fraction in the solution.*

Equation:

$$P_A = X_A P_A^\circ$$

where P_A is the partial pressure exerted by component A in the solution, P_A° is the vapor pressure of pure A, and X_A is the mole fraction of A in the solution. (Mole fraction is a concentration unit introduced in the chapter on gases.)

Recalling that the total pressure of a gaseous mixture is equal to the sum of partial pressures for all its components (Dalton's law of partial pressures), the total vapor pressure exerted by a solution containing i components is

Equation:

$$P_{\text{solution}} = \sum_i P_i = \sum_i X_i P_i^\circ$$

A nonvolatile substance is one whose vapor pressure is negligible ($P^\circ \approx 0$), and so the vapor pressure above a solution containing only nonvolatile solutes is due only to the solvent:

Equation:

$$P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}^\circ$$

Example:

Calculation of a Vapor Pressure

Compute the vapor pressure of an ideal solution containing 92.1 g of glycerin, $\text{C}_3\text{H}_5(\text{OH})_3$, and 184.4 g of ethanol, $\text{C}_2\text{H}_5\text{OH}$, at 40 °C. The vapor pressure of pure ethanol is 0.178 atm at 40 °C. Glycerin is essentially nonvolatile at this temperature.

Solution

Since the solvent is the only volatile component of this solution, its vapor pressure may be computed per Raoult's law as:

Equation:

$$P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}^\circ$$

First, calculate the molar amounts of each solution component using the provided mass data.

Equation:

$$\begin{aligned} 92.1 \text{ g } \text{C}_3\text{H}_5(\text{OH})_3 &\times \frac{1 \text{ mol } \text{C}_3\text{H}_5(\text{OH})_3}{92.094 \text{ g } \text{C}_3\text{H}_5(\text{OH})_3} = 1.00 \text{ mol } \text{C}_3\text{H}_5(\text{OH})_3 \\ 184.4 \text{ g } \text{C}_2\text{H}_5\text{OH} &\times \frac{1 \text{ mol } \text{C}_2\text{H}_5\text{OH}}{46.069 \text{ g } \text{C}_2\text{H}_5\text{OH}} = 4.000 \text{ mol } \text{C}_2\text{H}_5\text{OH} \end{aligned}$$

Next, calculate the mole fraction of the solvent (ethanol) and use Raoult's law to compute the solution's vapor pressure.

Equation:

$$\begin{aligned} X_{\text{C}_2\text{H}_5\text{OH}} &= \frac{4.000 \text{ mol}}{(1.00 \text{ mol} + 4.000 \text{ mol})} = 0.800 \\ P_{\text{solv}} &= X_{\text{solv}} P_{\text{solv}}^\circ = 0.800 \times 0.178 \text{ atm} = 0.142 \text{ atm} \end{aligned}$$

Check Your Learning

A solution contains 5.00 g of urea, $\text{CO}(\text{NH}_2)_2$ (a nonvolatile solute) and 0.100 kg of water. If the vapor pressure of pure water at 25 °C is 23.7 torr, what is the vapor pressure of the solution?

Note:

Answer:

23.4 torr

Elevation of the Boiling Point of a Solvent

As described in the chapter on liquids and solids, the *boiling point* of a liquid is the temperature at which its vapor pressure is equal to ambient atmospheric pressure. Since the vapor pressure of a solution is lowered due to the presence of nonvolatile solutes, it stands to reason that the solution's boiling point will subsequently be increased. Compared to pure solvent, a solution, therefore, will require a higher temperature to achieve any given vapor pressure, including one equivalent to that of the surrounding atmosphere. The increase in boiling point observed when nonvolatile solute is dissolved in a solvent, ΔT_b , is called **boiling point elevation** and is directly proportional to the molal concentration of solute species:

Equation:

$$\Delta T_b = K_b m$$

where K_b is the **boiling point elevation constant**, or the *ebullioscopic constant* and m is the molal concentration (molality) of all solute species.

Boiling point elevation constants are characteristic properties that depend on the identity of the solvent. Values of K_b for several solvents are listed in [\[link\]](#).

Boiling Point Elevation and Freezing Point Depression Constants for Several Solvents				
Solvent	Boiling Point (°C at 1 atm)	K_b (°C m^{-1})	Freezing Point (°C at 1 atm)	K_f (°C m^{-1})
water	100.0	0.512	0.0	1.86
hydrogen acetate	118.1	3.07	16.6	3.9
benzene	80.1	2.53	5.5	5.12
chloroform	61.26	3.63	−63.5	4.68
nitrobenzene	210.9	5.24	5.67	8.1

The extent to which the vapor pressure of a solvent is lowered and the boiling point is elevated depends on the total number of solute particles present in a given amount of solvent, not on the mass or size or chemical identities of the particles. A 1 m aqueous solution of sucrose (342 g/mol) and a 1

m aqueous solution of ethylene glycol (62 g/mol) will exhibit the same boiling point because each solution has one mole of solute particles (molecules) per kilogram of solvent.

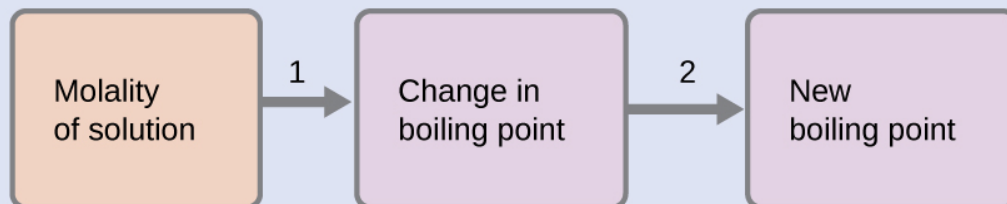
Example:

Calculating the Boiling Point of a Solution

What is the boiling point of a 0.33 m solution of a nonvolatile solute in benzene?

Solution

Use the equation relating boiling point elevation to solute molality to solve this problem in two steps.



Calculate the change in boiling point. **Equation:**

$$\Delta T_b = K_b m = 2.53\text{ }^{\circ}\text{C } m^{-1} \times 0.33\text{ } m = 0.83\text{ }^{\circ}\text{C}$$

Add the boiling point elevation to the pure solvent's boiling point. **Equation:**

$$\text{Boiling temperature} = 80.1\text{ }^{\circ}\text{C} + 0.83\text{ }^{\circ}\text{C} = 80.9\text{ }^{\circ}\text{C}$$

Check Your Learning

What is the boiling point of the antifreeze described in [\[link\]](#)?

Note:

Answer:

109.2 $^{\circ}\text{C}$

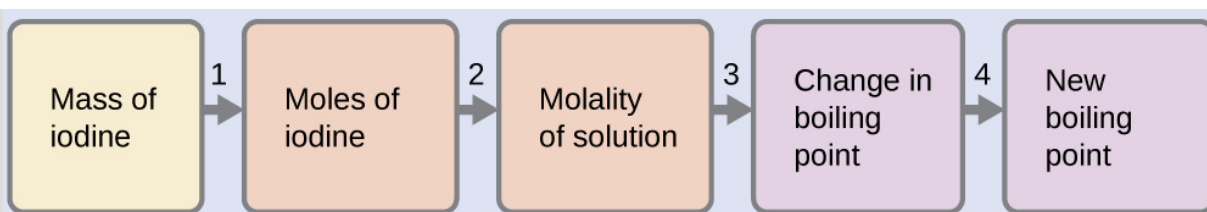
Example:

The Boiling Point of an Iodine Solution

Find the boiling point of a solution of 92.1 g of iodine, I_2 , in 800.0 g of chloroform, CHCl_3 , assuming that the iodine is nonvolatile and that the solution is ideal.

Solution

We can solve this problem using four steps.



Convert from grams to moles of iodine using the molar mass of iodine in the unit conversion factor. Result: 0.363 mol

Determine the molality of the solution from the number of moles of solute and the mass of solvent, in kilograms. Result: 0.454 m

Use the direct proportionality between the change in boiling point and molal concentration to determine how much the boiling point changes. Result: 1.65 °C

Determine the new boiling point from the boiling point of the pure solvent and the change. Result: 62.91 °C Check each result as a self-assessment.

Check Your Learning

What is the boiling point of a solution of 1.0 g of glycerin, $\text{C}_3\text{H}_5(\text{OH})_3$, in 47.8 g of water? Assume an ideal solution.

Note:

Answer:

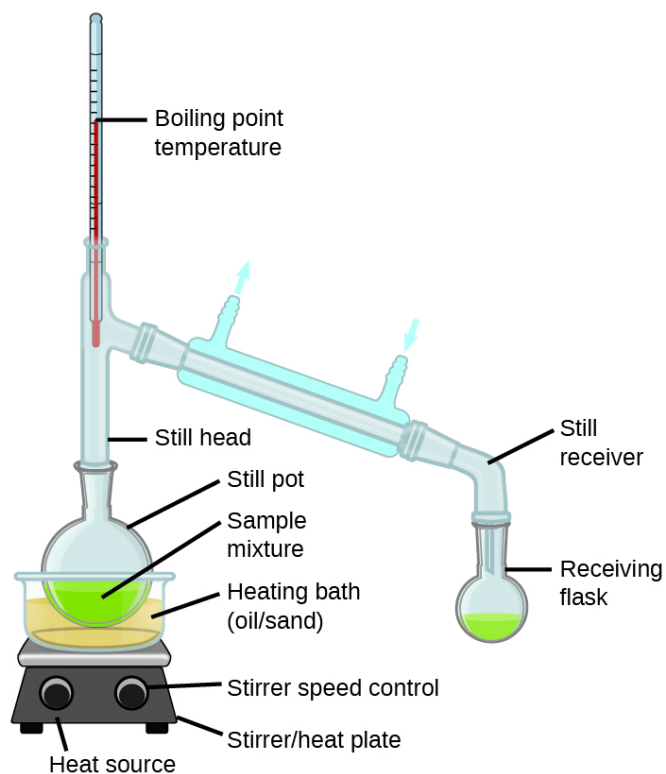
100.12 °C

Distillation of Solutions

Distillation is a technique for separating the components of mixtures that is widely applied in both in the laboratory and in industrial settings. It is used to refine petroleum, to isolate fermentation products, and to purify water. This separation technique involves the controlled heating of a sample mixture to selectively vaporize, condense, and collect one or more components of interest. A typical apparatus for laboratory-scale distillations is shown in [\[link\]](#).



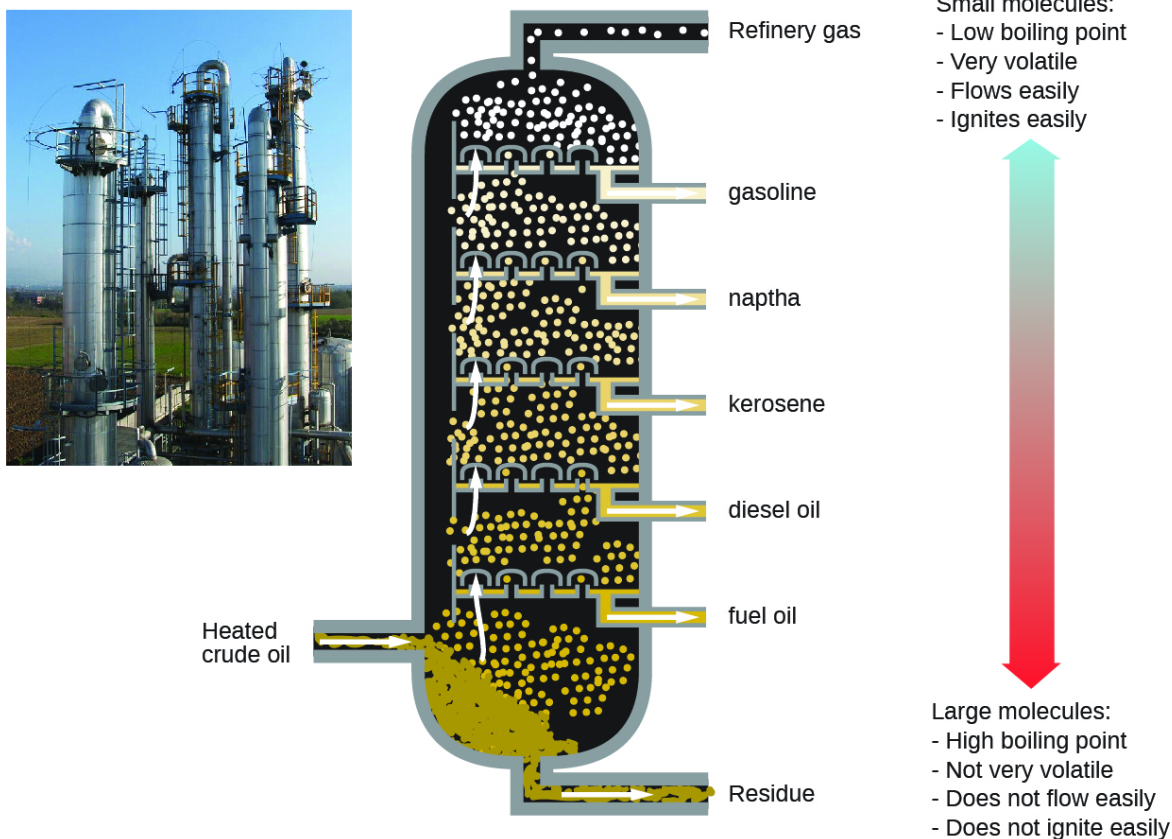
(a)



(b)

A typical laboratory distillation unit is shown in (a) a photograph and (b) a schematic diagram of the components. (credit a: modification of work by “Rifleman82”/Wikimedia commons; credit b: modification of work by “Slashme”/Wikimedia Commons)

Oil refineries use large-scale *fractional distillation* to separate the components of crude oil. The crude oil is heated to high temperatures at the base of a tall *fractionating column*, vaporizing many of the components that rise within the column. As vaporized components reach adequately cool zones during their ascent, they condense and are collected. The collected liquids are simpler mixtures of hydrocarbons and other petroleum compounds that are of appropriate composition for various applications (e.g., diesel fuel, kerosene, gasoline), as depicted in [\[link\]](#).



Crude oil is a complex mixture that is separated by large-scale fractional distillation to isolate various simpler mixtures.

Depression of the Freezing Point of a Solvent

Solutions freeze at lower temperatures than pure liquids. This phenomenon is exploited in “de-icing” schemes that use salt ([link](#)), calcium chloride, or urea to melt ice on roads and sidewalks, and in the use of ethylene glycol as an “antifreeze” in automobile radiators. Seawater freezes at a lower temperature than fresh water, and so the Arctic and Antarctic oceans remain unfrozen even at temperatures below 0 °C (as do the body fluids of fish and other cold-blooded sea animals that live in these oceans).



Rock salt (NaCl), calcium chloride (CaCl₂), or a mixture of the two are used to melt ice. (credit: modification of work by Eddie Welker)

The decrease in freezing point of a dilute solution compared to that of the pure solvent, ΔT_f , is called the **freezing point depression** and is directly proportional to the molal concentration of the solute
Equation:

$$\Delta T_f = K_f m$$

where m is the molal concentration of the solute and K_f is called the **freezing point depression constant** (or *cryoscopic constant*). Just as for boiling point elevation constants, these are characteristic properties whose values depend on the chemical identity of the solvent. Values of K_f for several solvents are listed in [\[link\]](#).

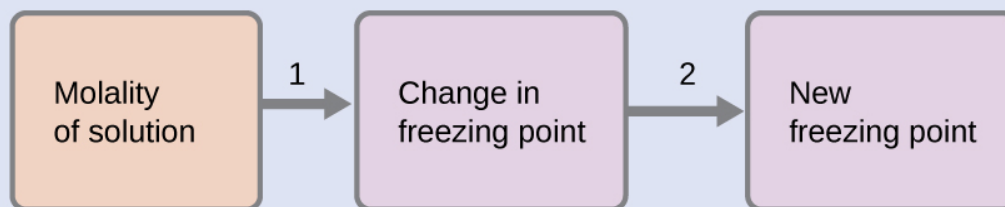
Example:

Calculation of the Freezing Point of a Solution

What is the freezing point of the 0.33 m solution of a nonvolatile nonelectrolyte solute in benzene described in [\[link\]](#)?

Solution

Use the equation relating freezing point depression to solute molality to solve this problem in two steps.



Calculate the change in freezing point. **Equation:**

$$\Delta T_f = K_f m = 5.12\text{ }^{\circ}\text{C } m^{-1} \times 0.33\text{ } m = 1.7\text{ }^{\circ}\text{C}$$

Subtract the freezing point change observed from the pure solvent's freezing point. **Equation:**

$$\text{Freezing Temperature} = 5.5\text{ }^{\circ}\text{C} - 1.7\text{ }^{\circ}\text{C} = 3.8\text{ }^{\circ}\text{C}$$

Check Your Learning

What is the freezing point of a 1.85 *m* solution of a nonvolatile nonelectrolyte solute in nitrobenzene?

Note:

Answer:

−9.3 °C

Note:

Colligative Properties and De-Icing

Sodium chloride and its group 2 analogs calcium and magnesium chloride are often used to de-ice roadways and sidewalks, due to the fact that a solution of any one of these salts will have a freezing point lower than 0 °C, the freezing point of pure water. The group 2 metal salts are frequently mixed with the cheaper and more readily available sodium chloride (“rock salt”) for use on roads, since they tend to be somewhat less corrosive than the NaCl, and they provide a larger depression of the freezing point, since they dissociate to yield three particles per formula unit, rather than two particles like the sodium chloride.

Because these ionic compounds tend to hasten the corrosion of metal, they would not be a wise choice to use in antifreeze for the radiator in your car or to de-ice a plane prior to takeoff. For these applications, covalent compounds, such as ethylene or propylene glycol, are often used. The glycols used in radiator fluid not only lower the freezing point of the liquid, but they elevate the boiling point, making the fluid useful in both winter and summer. Heated glycols are often sprayed onto the surface of airplanes prior to takeoff in inclement weather in the winter to remove ice that has already formed and prevent the formation of more ice, which would be particularly dangerous if formed on the control surfaces of the aircraft ([link](#)).



(a)

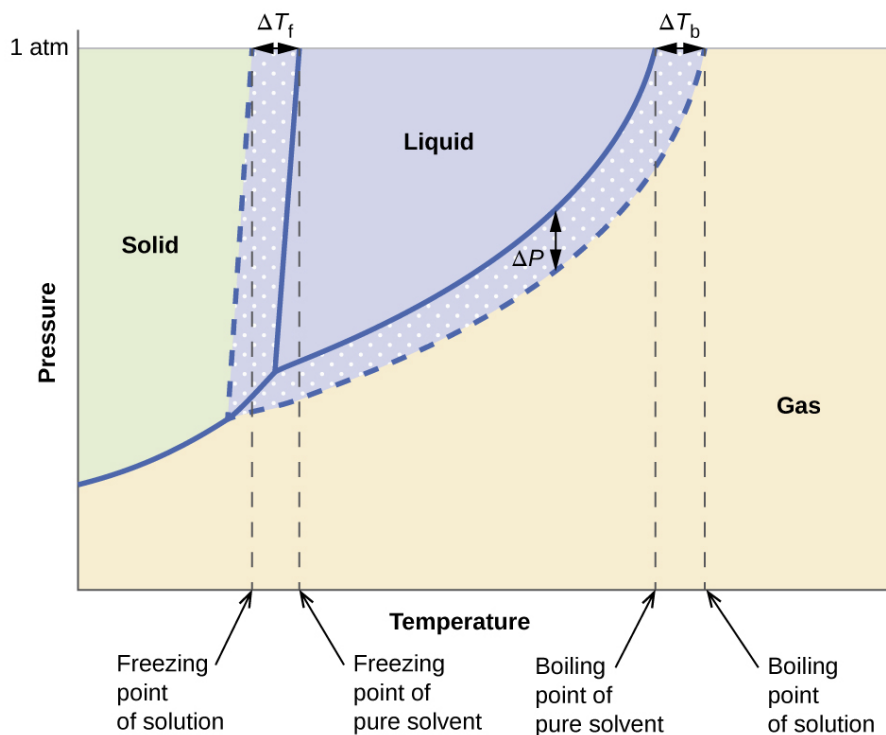


(b)

Freezing point depression is exploited to remove ice from (a) roadways and (b) the control surfaces of aircraft.

Phase Diagram for an Aqueous Solution of a Nonelectrolyte

The colligative effects on vapor pressure, boiling point, and freezing point described in the previous section are conveniently summarized by comparing the phase diagrams for a pure liquid and a solution derived from that liquid. Phase diagrams for water and an aqueous solution are shown in [\[link\]](#).



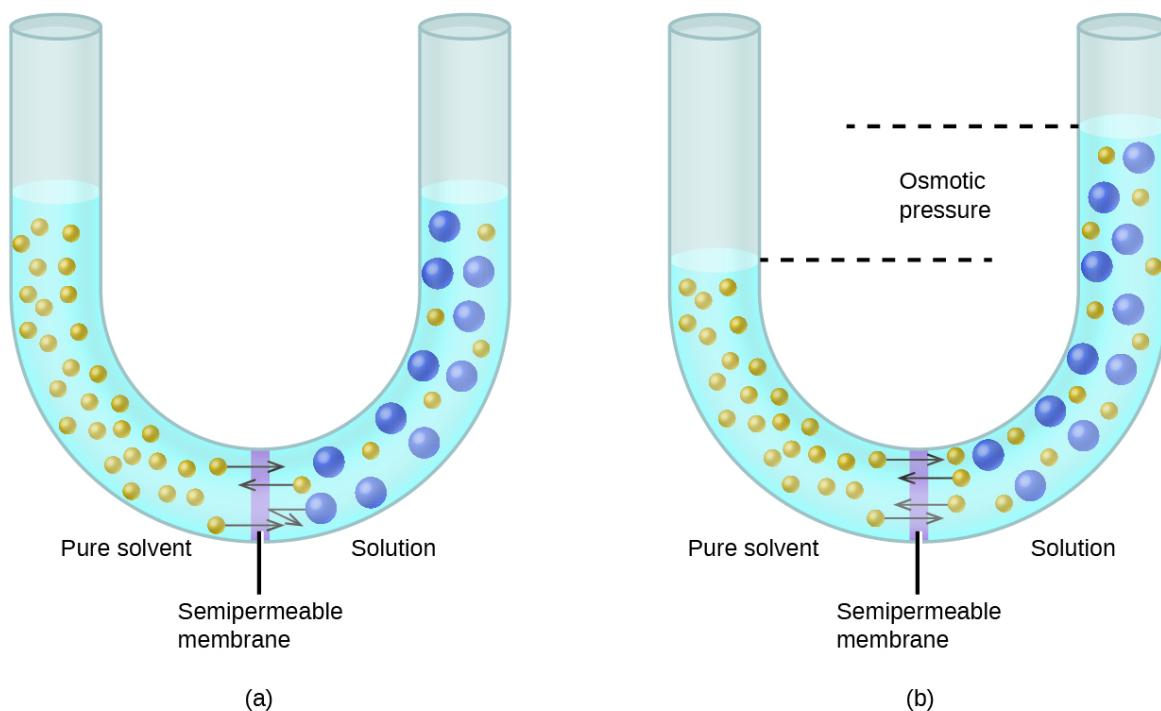
These phase diagrams show water (solid curves) and an aqueous solution of nonelectrolyte (dashed curves).

The liquid-vapor curve for the solution is located *beneath* the corresponding curve for the solvent, depicting the vapor pressure *lowering*, ΔP , that results from the dissolution of nonvolatile solute. Consequently, at any given pressure, the solution's boiling point is observed at a higher temperature than that for the pure solvent, reflecting the boiling point elevation, ΔT_b , associated with the presence of nonvolatile solute. The solid-liquid curve for the solution is displaced left of that for the pure solvent, representing the freezing point depression, ΔT_f , that accompanies solution formation. Finally, notice that the solid-gas curves for the solvent and its solution are identical. This is the case for many solutions comprising liquid solvents and nonvolatile solutes. Just as for vaporization, when a solution of this sort is frozen, it is actually just the *solvent* molecules that undergo the liquid-to-solid transition, forming pure solid solvent that excludes solute species. The solid and gaseous phases, therefore, are composed of solvent only, and so transitions between these phases are not subject to colligative effects.

Osmosis and Osmotic Pressure of Solutions

A number of natural and synthetic materials exhibit *selective permeation*, meaning that only molecules or ions of a certain size, shape, polarity, charge, and so forth, are capable of passing through (permeating) the material. Biological cell membranes provide elegant examples of selective permeation in nature, while dialysis tubing used to remove metabolic wastes from blood is a more simplistic technological example. Regardless of how they may be fabricated, these materials are generally referred to as **semipermeable membranes**.

Consider the apparatus illustrated in [\[link\]](#), in which samples of pure solvent and a solution are separated by a membrane that only solvent molecules may permeate. Solvent molecules will diffuse across the membrane in both directions. Since the concentration of *solvent* is greater in the pure solvent than the solution, these molecules will diffuse from the solvent side of the membrane to the solution side at a faster rate than they will in the reverse direction. The result is a net transfer of solvent molecules from the pure solvent to the solution. Diffusion-driven transfer of solvent molecules through a semipermeable membrane is a process known as **osmosis**.



Osmosis results in the transfer of solvent molecules from a sample of low (or zero) solute concentration to a sample of higher solute concentration.

When osmosis is carried out in an apparatus like that shown in [\[link\]](#), the volume of the solution increases as it becomes diluted by accumulation of solvent. This causes the level of the solution to rise, increasing its hydrostatic pressure (due to the weight of the column of solution in the tube) and resulting in a faster transfer of solvent molecules back to the pure solvent side. When the pressure reaches a value that yields a reverse solvent transfer rate equal to the osmosis rate, bulk transfer of solvent ceases. This pressure is called the **osmotic pressure (Π)** of the solution. The osmotic pressure of a dilute solution is related to its solute molarity, M , and absolute temperature, T , according to the equation

Equation:

$$\Pi = MRT$$

where R is the universal gas constant.

Example:

Calculation of Osmotic Pressure

What is the osmotic pressure (atm) of a 0.30 M solution of glucose in water that is used for intravenous infusion at body temperature, 37 °C?

Solution

We can find the osmotic pressure, Π , using the formula $\Pi = MRT$, where T is on the Kelvin scale (310 K) and the value of R is expressed in appropriate units (0.08206 L atm/mol K).

Equation:

$$\begin{aligned}\Pi &= MRT \\ &= 0.03 \text{ mol/L} \times 0.08206 \text{ L atm/mol K} \times 310 \text{ K} \\ &= 7.6 \text{ atm}\end{aligned}$$

Check Your Learning

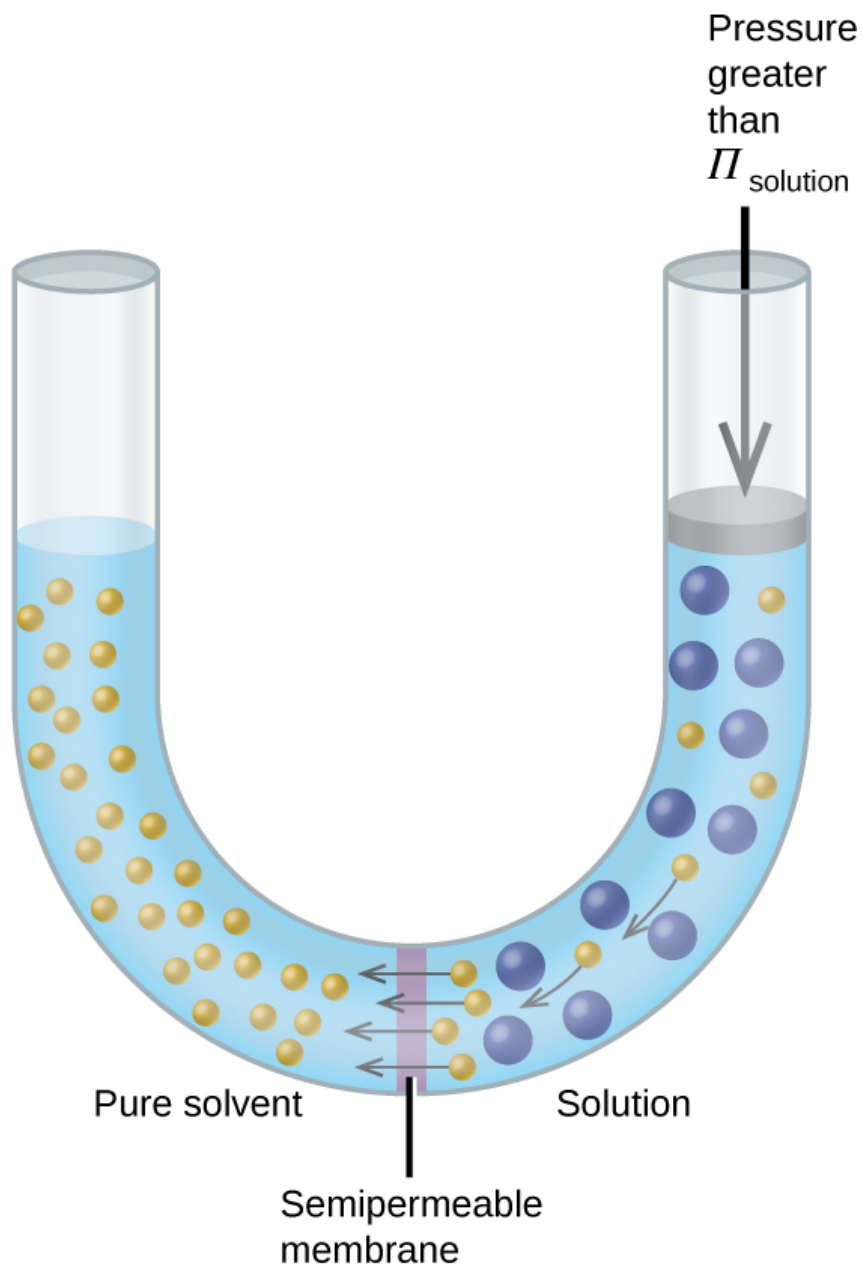
What is the osmotic pressure (atm) a solution with a volume of 0.750 L that contains 5.0 g of methanol, CH_3OH , in water at 37 °C?

Note:

Answer:

5.3 atm

If a solution is placed in an apparatus like the one shown in [\[link\]](#), applying pressure greater than the osmotic pressure of the solution reverses the osmosis and pushes solvent molecules from the solution into the pure solvent. This technique of reverse osmosis is used for large-scale desalination of seawater and on smaller scales to produce high-purity tap water for drinking.



Applying a pressure greater than the osmotic pressure of a solution will reverse osmosis. Solvent molecules from the solution are pushed into the pure solvent.

Note:

Reverse Osmosis Water Purification

In the process of osmosis, diffusion serves to move water through a semipermeable membrane from a less concentrated solution to a more concentrated solution. Osmotic pressure is the amount of

pressure that must be applied to the more concentrated solution to cause osmosis to stop. If greater pressure is applied, the water will go from the more concentrated solution to a less concentrated (more pure) solution. This is called reverse osmosis. Reverse osmosis (RO) is used to purify water in many applications, from desalination plants in coastal cities, to water-purifying machines in grocery stores ([\[link\]](#)), and smaller reverse-osmosis household units. With a hand-operated pump, small RO units can be used in third-world countries, disaster areas, and in lifeboats. Our military forces have a variety of generator-operated RO units that can be transported in vehicles to remote locations.



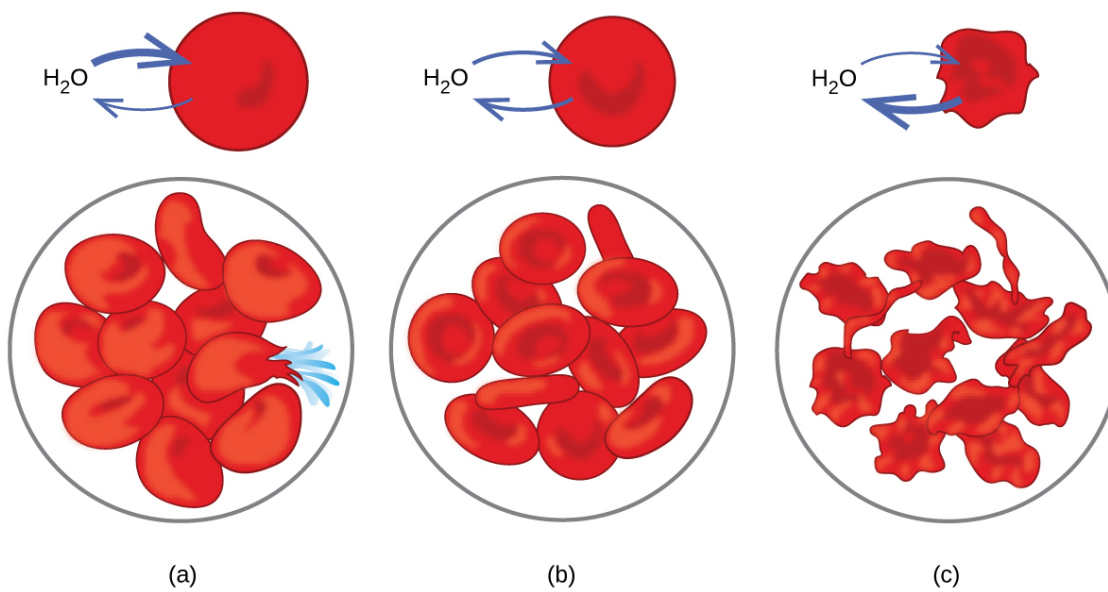
(a)



(b)

Reverse osmosis systems for purifying drinking water are shown here on (a) small and (b) large scales. (credit a: modification of work by Jerry Kirkhart; credit b: modification of work by Willard J. Lathrop)

Examples of osmosis are evident in many biological systems because cells are surrounded by semipermeable membranes. Carrots and celery that have become limp because they have lost water can be made crisp again by placing them in water. Water moves into the carrot or celery cells by osmosis. A cucumber placed in a concentrated salt solution loses water by osmosis and absorbs some salt to become a pickle. Osmosis can also affect animal cells. Solute concentrations are particularly important when solutions are injected into the body. Solute concentrations in body cell fluids and blood serum give these solutions an osmotic pressure of approximately 7.7 atm. Solutions injected into the body must have the same osmotic pressure as blood serum; that is, they should be **isotonic** with blood serum. If a less concentrated solution, a **hypotonic** solution, is injected in sufficient quantity to dilute the blood serum, water from the diluted serum passes into the blood cells by osmosis, causing the cells to expand and rupture. This process is called **hemolysis**. When a more concentrated solution, a **hypertonic** solution, is injected, the cells lose water to the more concentrated solution, shrivel, and possibly die in a process called **crenation**. These effects are illustrated in [\[link\]](#).



Red blood cell membranes are water permeable and will (a) swell and possibly rupture in a hypotonic solution; (b) maintain normal volume and shape in an isotonic solution; and (c) shrivel and possibly die in a hypertonic solution. (credit a/b/c: modifications of work by “LadyofHats”/Wikimedia commons)

Determination of Molar Masses

Osmotic pressure and changes in freezing point, boiling point, and vapor pressure are directly proportional to the concentration of solute present. Consequently, we can use a measurement of one of these properties to determine the molar mass of the solute from the measurements.

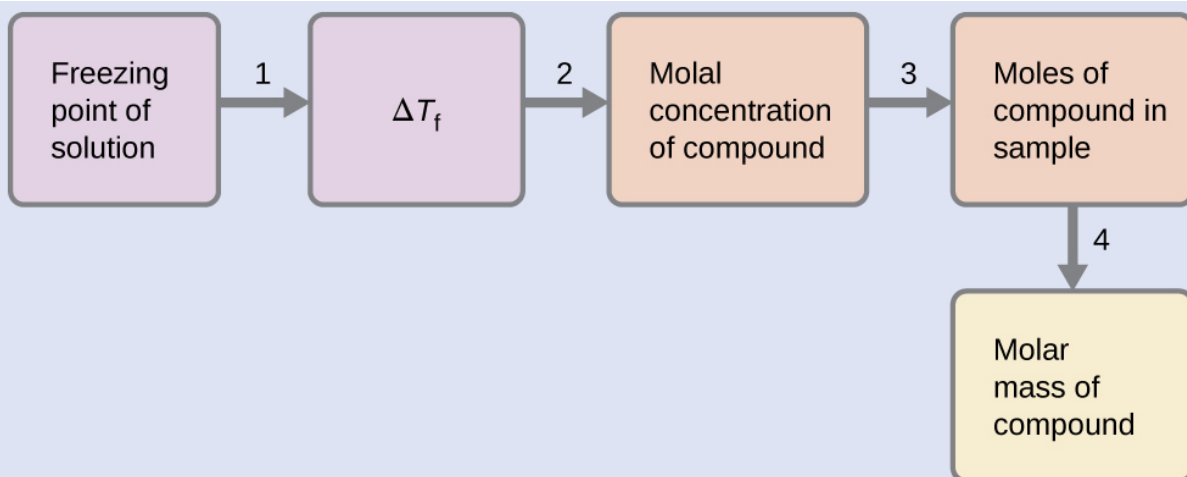
Example:

Determination of a Molar Mass from a Freezing Point Depression

A solution of 4.00 g of a nonelectrolyte dissolved in 55.0 g of benzene is found to freeze at 2.32 °C. What is the molar mass of this compound?

Solution

We can solve this problem using the following steps.



Determine the change in freezing point from the [link](#). **Equation:**
 observed freezing point and the freezing point of
 pure benzene

$$\Delta T_f = 5.5^\circ\text{C} - 2.32^\circ\text{C} = 3.2^\circ\text{C}$$

Determine the molal concentration from K_f , the freezing point depression constant for benzene [link](#), and ΔT_f . **Equation:**

$$\Delta T_f = K_f m$$

$$m = \frac{\Delta T_f}{K_f} = \frac{3.2^\circ\text{C}}{5.12^\circ\text{C } m^{-1}} = 0.63 m$$

Determine the number of moles of compound in the solution from the molal concentration and the mass of solvent used to make the solution. **Equation:**

Moles of solute = $\frac{0.63 \text{ mol solute}}{1.00 \text{ kg solvent}} \times 0.0550 \text{ kg solvent} = 0.035 \text{ mol}$

Determine the molar mass from the mass of the solute and the number of moles in that mass. **Equation:**

$$\text{Molar mass} = \frac{4.00 \text{ g}}{0.035 \text{ mol}} = 1.1 \times 10^2 \text{ g/mol}$$

Check Your Learning

A solution of 35.7 g of a nonelectrolyte in 220.0 g of chloroform has a boiling point of 64.5°C . What is the molar mass of this compound?

Note:

Answer:

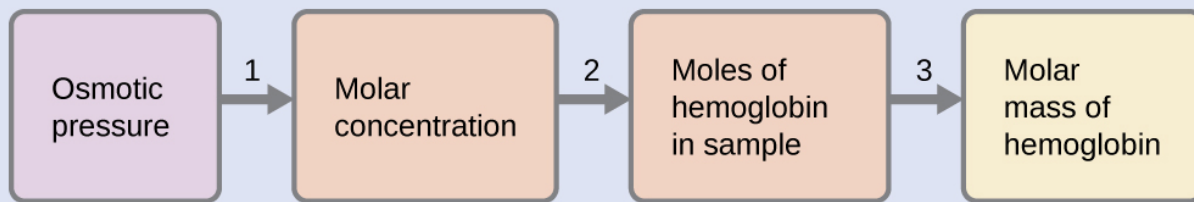
$$1.8 \times 10^2 \text{ g/mol}$$

Example:**Determination of a Molar Mass from Osmotic Pressure**

A 0.500 L sample of an aqueous solution containing 10.0 g of hemoglobin has an osmotic pressure of 5.9 torr at 22 °C. What is the molar mass of hemoglobin?

Solution

Here is one set of steps that can be used to solve the problem:



Convert the osmotic pressure to atmospheres, then determine the molar concentration from the osmotic pressure.

Equation:

$$\Pi = \frac{5.9 \text{ torr} \times 1 \text{ atm}}{760 \text{ torr}} = 7.8 \times 10^{-3} \text{ atm}$$

$$\Pi = MRT$$

$$M = \frac{\Pi}{RT} = \frac{7.8 \times 10^{-3} \text{ atm}}{(0.08206 \text{ L atm/mol K})(295 \text{ K})} = 3.2 \times 10^{-4} \text{ M}$$

Determine the number of moles of hemoglobin in the solution from the concentration and the volume of the solution.

Equation:

$$\text{moles of hemoglobin} = \frac{3.2 \times 10^{-4} \text{ mol}}{1 \text{ L solution}} \times 0.500 \text{ L solution} = 1.6 \times 10^{-4} \text{ mol}$$

Determine the molar mass from the mass of hemoglobin and the number of moles in that mass.

$$\text{molar mass} = \frac{10.0 \text{ g}}{1.6 \times 10^{-4} \text{ mol}} = 6.2 \times 10^4 \text{ g/mol}$$

Check Your Learning

What is the molar mass of a protein if a solution of 0.02 g of the protein in 25.0 mL of solution has an osmotic pressure of 0.56 torr at 25 °C?

Note:**Answer:**

$$3 \times 10^4 \text{ g/mol}$$

Colligative Properties of Electrolytes

As noted previously in this module, the colligative properties of a solution depend only on the number, not on the kind, of solute species dissolved. For example, 1 mole of any nonelectrolyte dissolved in 1 kilogram of solvent produces the same lowering of the freezing point as does 1 mole of any other nonelectrolyte. However, 1 mole of sodium chloride (an electrolyte) forms 2 moles of ions when dissolved in solution. Each individual ion produces the same effect on the freezing point as a single molecule does.

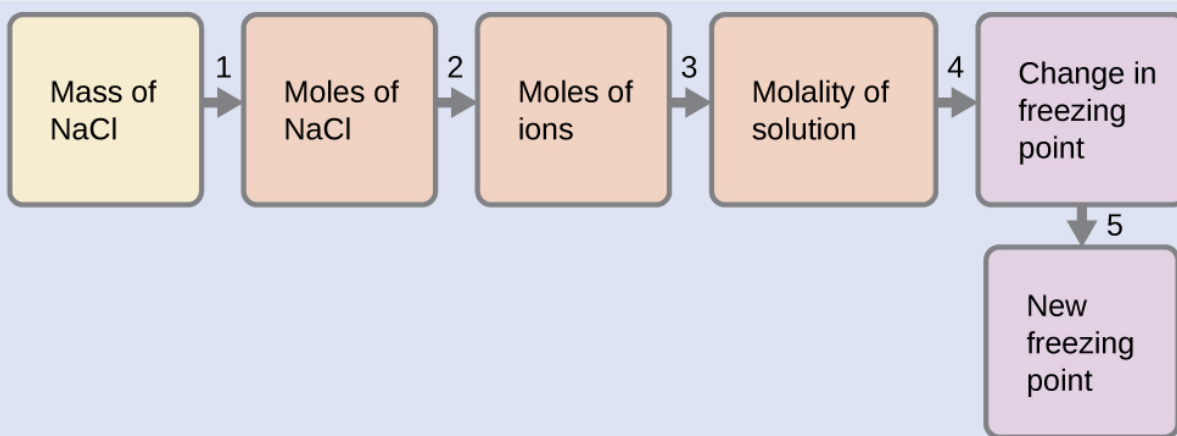
Example:

The Freezing Point of a Solution of an Electrolyte

The concentration of ions in seawater is approximately the same as that in a solution containing 4.2 g of NaCl dissolved in 125 g of water. Assume that each of the ions in the NaCl solution has the same effect on the freezing point of water as a nonelectrolyte molecule, and determine the freezing temperature the solution (which is approximately equal to the freezing temperature of seawater).

Solution

We can solve this problem using the following series of steps.



Convert from grams to moles of NaCl using the molar mass of NaCl in the unit conversion factor. Result: 0.072 mol NaCl

Determine the number of moles of ions present in the solution using the number of moles of ions in 1 mole of NaCl as the conversion factor (2 mol ions/1 mol NaCl). Result: 0.14 mol ions

Determine the molality of the ions in the solution from the number of moles of ions and the mass of solvent, in kilograms. Result: m 1.1

Use the direct proportionality between the change in freezing point and molal concentration to determine how much the freezing point changes. Result: 2.0°C

Determine the new freezing point from the freezing point of the pure solvent and the change. Result: -2.0°C Check each result as a self-assessment.

Check Your Learning

Assume that each of the ions in calcium chloride, CaCl_2 , has the same effect on the freezing point of water as a nonelectrolyte molecule. Calculate the freezing point of a solution of 0.724 g of CaCl_2 in 175 g of water.

Note:

Answer:

$-0.208\text{ }^{\circ}\text{C}$

Assuming complete dissociation, a 1.0 *m* aqueous solution of NaCl contains 2.0 mole of ions (1.0 mol Na^+ and 1.0 mol Cl^-) per each kilogram of water, and its freezing point depression is expected to be

Equation:

$$\Delta T_f = 2.0 \text{ mol ions/kg water} \times 1.86\text{ }^{\circ}\text{C kg water/mol ion} = 3.7\text{ }^{\circ}\text{C}.$$

When this solution is actually prepared and its freezing point depression measured, however, a value of $3.4\text{ }^{\circ}\text{C}$ is obtained. Similar discrepancies are observed for other ionic compounds, and the differences between the measured and expected colligative property values typically become more significant as solute concentrations increase. These observations suggest that the ions of sodium chloride (and other strong electrolytes) are not completely dissociated in solution.

To account for this and avoid the errors accompanying the assumption of total dissociation, an experimentally measured parameter named in honor of Nobel Prize-winning German chemist Jacobus Henricus van't Hoff is used. The **van't Hoff factor (*i*)** is defined as the ratio of solute particles in solution to the number of formula units dissolved:

Equation:

$$i = \frac{\text{moles of particles in solution}}{\text{moles of formula units dissolved}}$$

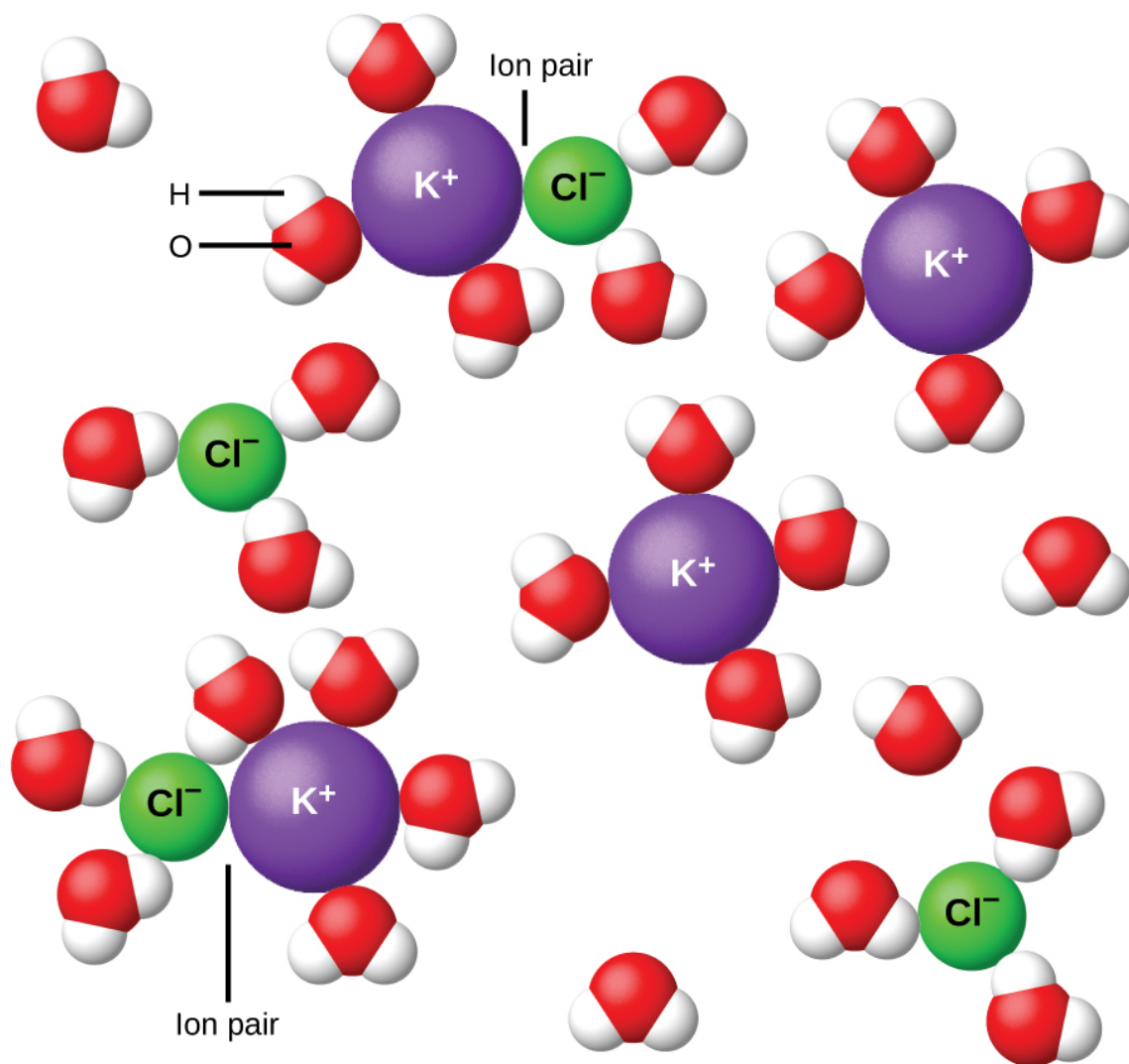
Values for measured van't Hoff factors for several solutes, along with predicted values assuming complete dissociation, are shown in [\[link\]](#).

Expected and Observed van't Hoff Factors for Several 0.050 *m* Aqueous Electrolyte Solutions

Expected and Observed van't Hoff Factor for Several 0.050 <i>m</i> Aqueous Electrolyte Solutions	Particles in Solution	<i>i</i> (Predicted)	<i>i</i> (Measured)
--	-----------------------	----------------------	---------------------

Electrolyte	Particles in Solution	<i>i</i> (Predicted)	<i>i</i> (Measured)
HCl	H ⁺ , Cl ⁻	2	1.9
NaCl	Na ⁺ , Cl ⁻	2	1.9
MgSO ₄	Mg ²⁺ , SO ₄ ²⁻	2	1.3
MgCl ₂	Mg ²⁺ , 2Cl ⁻	3	2.7
FeCl ₃	Fe ³⁺ , 3Cl ⁻	4	3.4
glucose ^[footnote] A nonelectrolyte shown for comparison.	C ₁₂ H ₂₂ O ₁₁	1	1.0

In 1923, the chemists Peter Debye and Erich Hückel proposed a theory to explain the apparent incomplete ionization of strong electrolytes. They suggested that although interionic attraction in an aqueous solution is very greatly reduced by solvation of the ions and the insulating action of the polar solvent, it is not completely nullified. The residual attractions prevent the ions from behaving as totally independent particles ([\[link\]](#)). In some cases, a positive and negative ion may actually touch, giving a solvated unit called an ion pair. Thus, the **activity**, or the effective concentration, of any particular kind of ion is less than that indicated by the actual concentration. Ions become more and more widely separated the more dilute the solution, and the residual interionic attractions become less and less. Thus, in extremely dilute solutions, the effective concentrations of the ions (their activities) are essentially equal to the actual concentrations. Note that the van't Hoff factors for the electrolytes in [\[link\]](#) are for 0.05 *m* solutions, at which concentration the value of *i* for NaCl is 1.9, as opposed to an ideal value of 2.



Ions become more and more widely separated the more dilute the solution, and the residual interionic attractions become less.

Key Concepts and Summary

Properties of a solution that depend only on the concentration of solute particles are called colligative properties. They include changes in the vapor pressure, boiling point, and freezing point of the solvent in the solution. The magnitudes of these properties depend only on the total concentration of solute particles in solution, not on the type of particles. The total concentration of solute particles in a solution also determines its osmotic pressure. This is the pressure that must be applied to the solution to prevent diffusion of molecules of pure solvent through a semipermeable membrane into the solution. Ionic compounds may not completely dissociate in solution due to activity effects, in which case observed colligative effects may be less than predicted.

Key Equations

- $(P_A = X_A P_A^\circ)$
- $P_{\text{solution}} = \sum_i P_i = \sum_i X_i P_i^\circ$
- $P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}^\circ$
- $\Delta T_b = K_b m$
- $\Delta T_f = K_f m$
- $\Pi = MRT$

Chemistry End of Chapter Exercises

Exercise:

Problem:

Which is/are part of the macroscopic domain of solutions and which is/are part of the microscopic domain: boiling point elevation, Henry's law, hydrogen bond, ion-dipole attraction, molarity, nonelectrolyte, nonstoichiometric compound, osmosis, solvated ion?

Exercise:

Problem:

What is the microscopic explanation for the macroscopic behavior illustrated in [\[link\]](#)?

Solution:

The strength of the bonds between like molecules is stronger than the strength between unlike molecules. Therefore, some regions will exist in which the water molecules will exclude oil molecules and other regions will exist in which oil molecules will exclude water molecules, forming a heterogeneous region.

Exercise:

Problem:

Sketch a qualitative graph of the pressure versus time for water vapor above a sample of pure water and a sugar solution, as the liquids evaporate to half their original volume.

Exercise:

Problem:

A solution of potassium nitrate, an electrolyte, and a solution of glycerin ($\text{C}_3\text{H}_5(\text{OH})_3$), a nonelectrolyte, both boil at 100.3°C . What other physical properties of the two solutions are identical?

Solution:

Both form homogeneous solutions; their boiling point elevations are the same, as are their lowering of vapor pressures. Osmotic pressure and the lowering of the freezing point are also the same for both solutions.

Exercise:**Problem:**

What are the mole fractions of H_3PO_4 and water in a solution of 14.5 g of H_3PO_4 in 125 g of water?

- (a) Outline the steps necessary to answer the question.
- (b) Answer the question.

Exercise:**Problem:**

What are the mole fractions of HNO_3 and water in a concentrated solution of nitric acid (68.0% HNO_3 by mass)?

- (a) Outline the steps necessary to answer the question.
- (b) Answer the question.

Solution:

- (a) Find number of moles of HNO_3 and H_2O in 100 g of the solution. Find the mole fractions for the components.
- (b) The mole fraction of HNO_3 is 0.378. The mole fraction of H_2O is 0.622.

Exercise:

Problem: Calculate the mole fraction of each solute and solvent:

- (a) 583 g of H_2SO_4 in 1.50 kg of water—the acid solution used in an automobile battery
- (b) 0.86 g of NaCl in 1.00×10^2 g of water—a solution of sodium chloride for intravenous injection
- (c) 46.85 g of codeine, $\text{C}_{18}\text{H}_{21}\text{NO}_3$, in 125.5 g of ethanol, $\text{C}_2\text{H}_5\text{OH}$
- (d) 25 g of I_2 in 125 g of ethanol, $\text{C}_2\text{H}_5\text{OH}$

Exercise:

Problem: Calculate the mole fraction of each solute and solvent:

- (a) 0.710 kg of sodium carbonate (washing soda), Na_2CO_3 , in 10.0 kg of water—a saturated solution at 0°C
 - (b) 125 g of NH_4NO_3 in 275 g of water—a mixture used to make an instant ice pack
 - (c) 25 g of Cl_2 in 125 g of dichloromethane, CH_2Cl_2
 - (d) 0.372 g of tetrahydropyridine, $\text{C}_5\text{H}_9\text{N}$, in 125 g of chloroform, CHCl_3
-

Solution:

(a) $X_{\text{Na}_2\text{CO}_3} = 0.0119$; $X_{\text{H}_2\text{O}} = 0.988$; (b) $X_{\text{NH}_4\text{NO}_3} = 0.0928$; $X_{\text{H}_2\text{O}} = 0.907$; (c) $X_{\text{Cl}_2} = 0.192$; $X_{\text{CH}_2\text{Cl}_2} = 0.808$; (d) $X_{\text{C}_5\text{H}_9\text{N}} = 0.00426$; $X_{\text{CHCl}_3} = 0.997$

Exercise:**Problem:**

Calculate the mole fractions of methanol, CH_3OH ; ethanol, $\text{C}_2\text{H}_5\text{OH}$; and water in a solution that is 40% methanol, 40% ethanol, and 20% water by mass. (Assume the data are good to two significant figures.)

Exercise:

Problem: What is the difference between a 1 *M* solution and a 1 *m* solution?

Solution:

In a 1 *M* solution, the mole is contained in exactly 1 L of solution. In a 1 *m* solution, the mole is contained in exactly 1 kg of solvent.

Exercise:**Problem:**

What is the molality of phosphoric acid, H_3PO_4 , in a solution of 14.5 g of H_3PO_4 in 125 g of water?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

Exercise:**Problem:**

What is the molality of nitric acid in a concentrated solution of nitric acid (68.0% HNO_3 by mass)?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

Solution:

(a) Determine the molar mass of HNO_3 . Determine the number of moles of acid in the solution. From the number of moles and the mass of solvent, determine the molality. (b) 33.7 *m*

Exercise:

Problem: Calculate the molality of each of the following solutions:

(a) 583 g of H_2SO_4 in 1.50 kg of water—the acid solution used in an automobile battery

(b) 0.86 g of NaCl in 1.00×10^2 g of water—a solution of sodium chloride for intravenous injection

(c) 46.85 g of codeine, $\text{C}_{18}\text{H}_{21}\text{NO}_3$, in 125.5 g of ethanol, $\text{C}_2\text{H}_5\text{OH}$

(d) 25 g of I_2 in 125 g of ethanol, $\text{C}_2\text{H}_5\text{OH}$

Exercise:

Problem: Calculate the molality of each of the following solutions:

(a) 0.710 kg of sodium carbonate (washing soda), Na_2CO_3 , in 10.0 kg of water—a saturated solution at 0°C

(b) 125 g of NH_4NO_3 in 275 g of water—a mixture used to make an instant ice pack

(c) 25 g of Cl_2 in 125 g of dichloromethane, CH_2Cl_2

(d) 0.372 g of tetrahydropyridine, $\text{C}_5\text{H}_9\text{N}$, in 125 g of chloroform, CHCl_3

Solution:

(a) $6.70 \times 10^{-1} m$; (b) $5.67 m$; (c) $2.8 m$; (d) $0.0358 m$

Exercise:

Problem:

The concentration of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, in normal spinal fluid is $\frac{75 \text{ mg}}{100 \text{ g}}$. What is the molality of the solution?

Exercise:

Problem:

A 13.0% solution of K_2CO_3 by mass has a density of 1.09 g/cm^3 . Calculate the molality of the solution.

Solution:

$1.08 m$

Exercise:

Problem:

Why does 1 mol of sodium chloride depress the freezing point of 1 kg of water almost twice as much as 1 mol of glycerin?

Exercise:

Problem:

What is the boiling point of a solution of 115.0 g of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, in 350.0 g of water?

(a) Outline the steps necessary to answer the question

(b) Answer the question

Solution:

(a) Determine the molar mass of sucrose; determine the number of moles of sucrose in the solution; convert the mass of solvent to units of kilograms; from the number of moles and the mass of solvent, determine the molality; determine the difference between the boiling point of water and the boiling point of the solution; determine the new boiling point. (b) 100.5 °C

Exercise:

Problem:

What is the boiling point of a solution of 9.04 g of I₂ in 75.5 g of benzene, assuming the I₂ is nonvolatile?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

Exercise:

Problem:

What is the freezing temperature of a solution of 115.0 g of sucrose, C₁₂H₂₂O₁₁, in 350.0 g of water, which freezes at 0.0 °C when pure?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

Solution:

(a) Determine the molar mass of sucrose; determine the number of moles of sucrose in the solution; convert the mass of solvent to units of kilograms; from the number of moles and the mass of solvent, determine the molality; determine the difference between the freezing temperature of water and the freezing temperature of the solution; determine the new freezing temperature. (b) -1.8 °C

Exercise:

Problem: What is the freezing point of a solution of 9.04 g of I₂ in 75.5 g of benzene?

(a) Outline the steps necessary to answer the following question.

(b) Answer the question.

Exercise:

Problem:

What is the osmotic pressure of an aqueous solution of 1.64 g of Ca(NO₃)₂ in water at 25 °C? The volume of the solution is 275 mL.

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

Solution:

(a) Determine the molar mass of $\text{Ca}(\text{NO}_3)_2$; determine the number of moles of $\text{Ca}(\text{NO}_3)_2$ in the solution; determine the number of moles of ions in the solution; determine the molarity of ions, then the osmotic pressure. (b) 2.67 atm

Exercise:

Problem:

What is osmotic pressure of a solution of bovine insulin (molar mass, 5700 g mol^{-1}) at 18°C if 100.0 mL of the solution contains 0.103 g of the insulin?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

Exercise:

Problem:

What is the molar mass of a solution of 5.00 g of a compound in 25.00 g of carbon tetrachloride (bp 76.8°C ; $K_b = 5.02^\circ\text{C}/m$) that boils at 81.5°C at 1 atm?

(a) Outline the steps necessary to answer the question.

(b) Solve the problem.

Solution:

(a) Determine the molal concentration from the change in boiling point and K_b ; determine the moles of solute in the solution from the molal concentration and mass of solvent; determine the molar mass from the number of moles and the mass of solute. (b) $2.1 \times 10^2 \text{ g mol}^{-1}$

Exercise:

Problem:

A sample of an organic compound (a nonelectrolyte) weighing 1.35 g lowered the freezing point of 10.0 g of benzene by 3.66°C . Calculate the molar mass of the compound.

Exercise:

Problem:

A 1.0 *m* solution of HCl in benzene has a freezing point of 0.4°C . Is HCl an electrolyte in benzene? Explain.

Solution:

No. Pure benzene freezes at 5.5°C , and so the observed freezing point of this solution is depressed by $\Delta T_f = 5.5 - 0.4 = 5.1^\circ\text{C}$. The value computed, assuming no ionization of HCl, is

$\Delta T_f = (1.0\text{ m})(5.14\text{ }^\circ\text{C}/m) = 5.1\text{ }^\circ\text{C}$. Agreement of these values supports the assumption that HCl is not ionized.

Exercise:

Problem:

A solution contains 5.00 g of urea, $\text{CO}(\text{NH}_2)_2$, a nonvolatile compound, dissolved in 0.100 kg of water. If the vapor pressure of pure water at 25 $^\circ\text{C}$ is 23.7 torr, what is the vapor pressure of the solution?

Exercise:

Problem:

A 12.0-g sample of a nonelectrolyte is dissolved in 80.0 g of water. The solution freezes at $-1.94\text{ }^\circ\text{C}$. Calculate the molar mass of the substance.

Solution:

144 g mol^{-1}

Exercise:

Problem:

Arrange the following solutions in order by their decreasing freezing points: 0.1 m Na_3PO_4 , 0.1 m $\text{C}_2\text{H}_5\text{OH}$, 0.01 m CO_2 , 0.15 m NaCl , and 0.2 m CaCl_2 .

Exercise:

Problem:

Calculate the boiling point elevation of 0.100 kg of water containing 0.010 mol of NaCl , 0.020 mol of Na_2SO_4 , and 0.030 mol of MgCl_2 , assuming complete dissociation of these electrolytes.

Solution:

$0.870\text{ }^\circ\text{C}$

Exercise:

Problem:

How could you prepare a 3.08 m aqueous solution of glycerin, $\text{C}_3\text{H}_8\text{O}_3$? What is the freezing point of this solution?

Exercise:

Problem:

A sample of sulfur weighing 0.210 g was dissolved in 17.8 g of carbon disulfide, CS_2 ($K_b = 2.43\text{ }^\circ\text{C}/m$). If the boiling point elevation was $0.107\text{ }^\circ\text{C}$, what is the formula of a sulfur molecule in carbon disulfide?

Solution:

S₈

Exercise:

Problem:

In a significant experiment performed many years ago, 5.6977 g of cadmium iodide in 44.69 g of water raised the boiling point 0.181 °C. What does this suggest about the nature of a solution of CdI₂?

Exercise:

Problem:

Lysozyme is an enzyme that cleaves cell walls. A 0.100-L sample of a solution of lysozyme that contains 0.0750 g of the enzyme exhibits an osmotic pressure of 1.32×10^{-3} atm at 25 °C. What is the molar mass of lysozyme?

Solution:

$$1.39 \times 10^4 \text{ g mol}^{-1}$$

Exercise:

Problem:

The osmotic pressure of a solution containing 7.0 g of insulin per liter is 23 torr at 25 °C. What is the molar mass of insulin?

Exercise:

Problem:

The osmotic pressure of human blood is 7.6 atm at 37 °C. What mass of glucose, C₆H₁₂O₆, is required to make 1.00 L of aqueous solution for intravenous feeding if the solution must have the same osmotic pressure as blood at body temperature, 37 °C?

Solution:

54 g

Exercise:

Problem:

What is the freezing point of a solution of dibromobenzene, C₆H₄Br₂, in 0.250 kg of benzene, if the solution boils at 83.5 °C?

Exercise:

Problem:

What is the boiling point of a solution of NaCl in water if the solution freezes at −0.93 °C?

Solution:

100.26 °C

Exercise:**Problem:**

The sugar fructose contains 40.0% C, 6.7% H, and 53.3% O by mass. A solution of 11.7 g of fructose in 325 g of ethanol has a boiling point of 78.59 °C. The boiling point of ethanol is 78.35 °C, and K_b for ethanol is 1.20 °C/m. What is the molecular formula of fructose?

Exercise:**Problem:**

The vapor pressure of methanol, CH_3OH , is 94 torr at 20 °C. The vapor pressure of ethanol, $\text{C}_2\text{H}_5\text{OH}$, is 44 torr at the same temperature.

- (a) Calculate the mole fraction of methanol and of ethanol in a solution of 50.0 g of methanol and 50.0 g of ethanol.
- (b) Ethanol and methanol form a solution that behaves like an ideal solution. Calculate the vapor pressure of methanol and of ethanol above the solution at 20 °C.
- (c) Calculate the mole fraction of methanol and of ethanol in the vapor above the solution.

Solution:

(a) $X_{\text{CH}_3\text{OH}} = 0.590$; $X_{\text{C}_2\text{H}_5\text{OH}} = 0.410$; (b) Vapor pressures are: CH_3OH : 55 torr; $\text{C}_2\text{H}_5\text{OH}$: 18 torr; (c) CH_3OH : 0.75; $\text{C}_2\text{H}_5\text{OH}$: 0.25

Exercise:**Problem:**

The triple point of air-free water is defined as 273.16 K. Why is it important that the water be free of air?

Exercise:**Problem:**

Meat can be classified as fresh (not frozen) even though it is stored at -1 °C. Why wouldn't meat freeze at this temperature?

Solution:

The ions and compounds present in the water in the beef lower the freezing point of the beef below -1 °C.

Exercise:**Problem:**

An organic compound has a composition of 93.46% C and 6.54% H by mass. A solution of 0.090 g of this compound in 1.10 g of camphor melts at 158.4 °C. The melting point of pure camphor is 178.4 °C. K_f for camphor is 37.7 °C/m. What is the molecular formula of the solute? Show your calculations.

Exercise:**Problem:**

A sample of HgCl_2 weighing 9.41 g is dissolved in 32.75 g of ethanol, $\text{C}_2\text{H}_5\text{OH}$ ($K_b = 1.20\text{ }^\circ\text{C}/m$). The boiling point elevation of the solution is $1.27\text{ }^\circ\text{C}$. Is HgCl_2 an electrolyte in ethanol? Show your calculations.

Solution:

$$\Delta bp = K_b m = (1.20\text{ }^\circ\text{C}/m) \left(\frac{9.41\text{ g} \times \frac{1\text{ mol HgCl}_2}{271.496\text{ g}}}{0.03275\text{ kg}} \right) = 1.27\text{ }^\circ\text{C}$$

The observed change equals the theoretical change; therefore, no dissociation occurs.

Exercise:**Problem:**

A salt is known to be an alkali metal fluoride. A quick approximate determination of freezing point indicates that 4 g of the salt dissolved in 100 g of water produces a solution that freezes at about $-1.4\text{ }^\circ\text{C}$. What is the formula of the salt? Show your calculations.

Glossary

boiling point elevation

elevation of the boiling point of a liquid by addition of a solute

boiling point elevation constant

the proportionality constant in the equation relating boiling point elevation to solute molality; also known as the ebullioscopic constant

colligative property

property of a solution that depends only on the concentration of a solute species

crenation

process whereby biological cells become shriveled due to loss of water by osmosis

freezing point depression

lowering of the freezing point of a liquid by addition of a solute

freezing point depression constant

(also, cryoscopic constant) proportionality constant in the equation relating freezing point depression to solute molality

hemolysis

rupture of red blood cells due to the accumulation of excess water by osmosis

hypertonic

of greater osmotic pressure

hypotonic

of less osmotic pressure

ion pair

solvated anion/cation pair held together by moderate electrostatic attraction

isotonic

of equal osmotic pressure

molality (m)

a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms

osmosis

diffusion of solvent molecules through a semipermeable membrane

osmotic pressure (Π)

opposing pressure required to prevent bulk transfer of solvent molecules through a semipermeable membrane

Raoult's law

the partial pressure exerted by a solution component is equal to the product of the component's mole fraction in the solution and its equilibrium vapor pressure in the pure state

semipermeable membrane

a membrane that selectively permits passage of certain ions or molecules

van't Hoff factor (i)

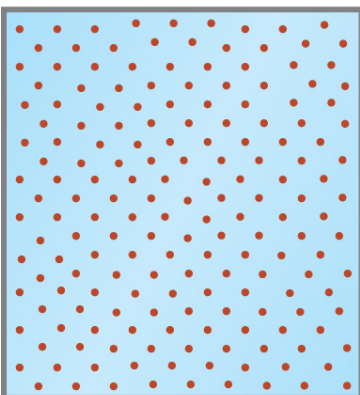
the ratio of the number of moles of particles in a solution to the number of moles of formula units dissolved in the solution

Colloids

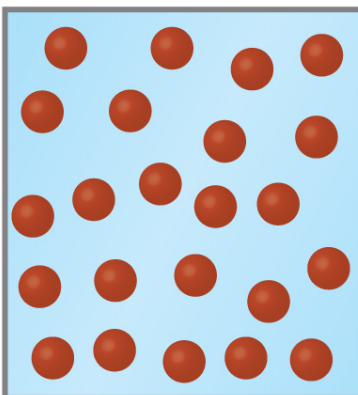
By the end of this section, you will be able to:

- Describe the composition and properties of colloidal dispersions
- List and explain several technological applications of colloids

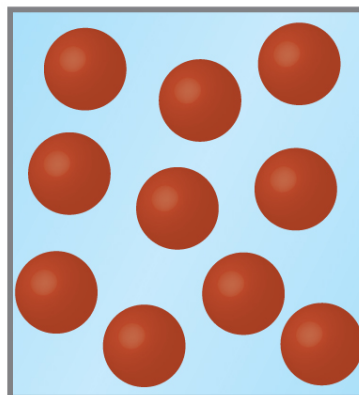
As a child, you may have made suspensions such as mixtures of mud and water, flour and water, or a suspension of solid pigments in water, known as tempera paint. These suspensions are heterogeneous mixtures composed of relatively large particles that are visible (or that can be seen with a magnifying glass). They are cloudy, and the suspended particles settle out after mixing. On the other hand, when we make a solution, we prepare a homogeneous mixture in which no settling occurs and in which the dissolved species are molecules or ions. Solutions exhibit completely different behavior from suspensions. A solution may be colored, but it is transparent, the molecules or ions are invisible, and they do not settle out on standing. A group of mixtures called **colloids** (or **colloidal dispersions**) exhibit properties intermediate between those of suspensions and solutions ([\[link\]](#)). The particles in a colloid are larger than most simple molecules; however, colloidal particles are small enough that they do not settle out upon standing.



(a)



(b)



(c)

(a) A solution is a homogeneous mixture that appears clear, such as the saltwater in this aquarium. (b) In a colloid, such as milk, the particles are

much larger but remain dispersed and do not settle. (c) A suspension, such as mud, is a heterogeneous mixture of suspended particles that appears cloudy and in which the particles can settle. (credit a photo: modification of work by Adam Wimsatt; credit b photo: modification of work by Melissa Wiese; credit c photo: modification of work by Peter Burgess)

The particles in a colloid are large enough to scatter light, a phenomenon called the **Tyndall effect**. This can make colloidal mixtures appear cloudy or opaque, such as the searchlight beams shown in [\[link\]](#). Clouds are colloidal mixtures. They are composed of water droplets that are much larger than molecules, but that are small enough that they do not settle out.



The paths of searchlight beams are made visible when light is scattered by colloidal-size particles in the air (fog, smoke, etc.). (credit: “Bahman”/Wikimedia Commons)

The term “colloid”—from the Greek words *kolla*, meaning “glue,” and *eidos*, meaning “like”—was first used in 1861 by Thomas Graham to classify mixtures such as starch in water and gelatin. Many colloidal particles are aggregates of hundreds or thousands of molecules, but others (such as proteins and polymer molecules) consist of a single extremely large molecule. The protein and synthetic polymer molecules that form colloids may have molecular masses ranging from a few thousand to many million atomic mass units.

Analogous to the identification of solution components as “solute” and “solvent,” the components of a colloid are likewise classified according to their relative amounts. The particulate component typically present in a relatively minor amount is called the **dispersed phase** and the substance or solution throughout which the particulate is dispersed is called the **dispersion medium**. Colloids may involve virtually any combination of physical states (gas in liquid, liquid in solid, solid in gas, etc.), as illustrated by the examples of colloidal systems given in [\[link\]](#).

Examples of Colloidal Systems			
Dispersed Phase	Dispersion Medium	Common Examples	Name
solid	gas	smoke, dust	—
solid	liquid	starch in water, some inks, paints, milk of magnesia	sol
solid	solid	some colored gems, some alloys	—
liquid	gas	clouds, fogs, mists, sprays	aerosol
liquid	liquid	milk, mayonnaise, butter	emulsion

Examples of Colloidal Systems			
Dispersed Phase	Dispersion Medium	Common Examples	Name
liquid	solid	jellies, gels, pearl, opal (H ₂ O in SiO ₂)	gel
gas	liquid	foams, whipped cream, beaten egg whites	foam
gas	solid	pumice, floating soaps	—

Preparation of Colloidal Systems

We can prepare a colloidal system by producing particles of colloidal dimensions and distributing these particles throughout a dispersion medium. Particles of colloidal size are formed by two methods:

1. Dispersion methods: that is, by breaking down larger particles. For example, paint pigments are produced by dispersing large particles by grinding in special mills.
2. Condensation methods: that is, growth from smaller units, such as molecules or ions. For example, clouds form when water molecules condense and form very small droplets.

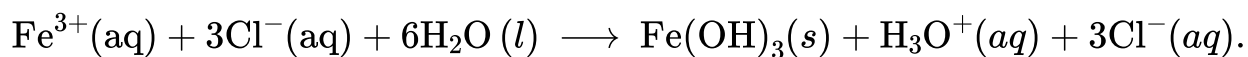
A few solid substances, when brought into contact with water, disperse spontaneously and form colloidal systems. Gelatin, glue, starch, and dehydrated milk powder behave in this manner. The particles are already of colloidal size; the water simply disperses them. Powdered milk particles of colloidal size are produced by dehydrating milk spray. Some atomizers produce colloidal dispersions of a liquid in air.

We can prepare an **emulsion** by shaking together or blending two immiscible liquids. This breaks one liquid into droplets of colloidal size, which then disperse throughout the other liquid. Oil spills in the ocean may be difficult to clean up, partly because wave action can cause the oil and water to form an emulsion. In many emulsions, however, the dispersed phase tends to coalesce, form large drops, and separate. Therefore, emulsions are usually stabilized by an

emulsifying agent, a substance that inhibits the coalescence of the dispersed liquid. For example, a little soap will stabilize an emulsion of kerosene in water. Milk is an emulsion of butterfat in water, with the protein casein as the emulsifying agent. Mayonnaise is an emulsion of oil in vinegar, with egg yolk components as the emulsifying agents.

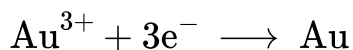
Condensation methods form colloidal particles by aggregation of molecules or ions. If the particles grow beyond the colloidal size range, drops or precipitates form, and no colloidal system results. Clouds form when water molecules aggregate and form colloid-sized particles. If these water particles coalesce to form adequately large water drops of liquid water or crystals of solid water, they settle from the sky as rain, sleet, or snow. Many condensation methods involve chemical reactions. We can prepare a red colloidal suspension of iron(III) hydroxide by mixing a concentrated solution of iron(III) chloride with hot water:

Equation:



A colloidal gold sol results from the reduction of a very dilute solution of gold(III) chloride by a reducing agent such as formaldehyde, tin(II) chloride, or iron(II) sulfate:

Equation:

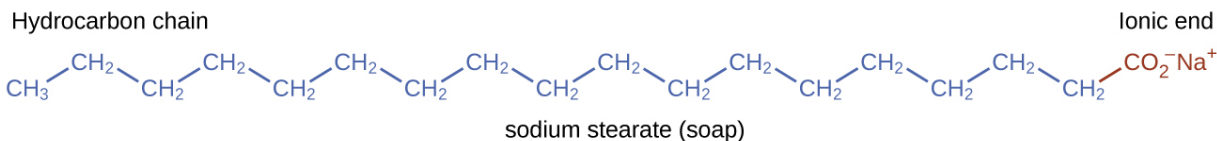


Some gold sols prepared in 1857 are still intact (the particles have not coalesced and settled), illustrating the long-term stability of many colloids.

Soaps and Detergents

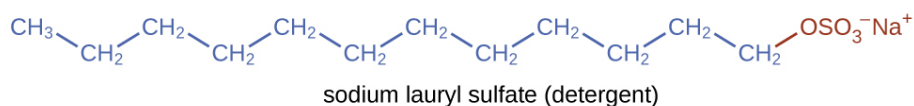
Pioneers made soap by boiling fats with a strongly basic solution made by leaching potassium carbonate, K_2CO_3 , from wood ashes with hot water. Animal fats contain polyesters of fatty acids (long-chain carboxylic acids). When animal fats are treated with a base like potassium carbonate or sodium hydroxide, glycerol and salts of fatty acids such as palmitic, oleic, and stearic acid are formed. The salts of fatty acids are called *soaps*. The sodium salt of stearic acid, sodium stearate, has the formula $\text{C}_{17}\text{H}_{35}\text{CO}_2\text{Na}$ and contains an uncharged

nonpolar hydrocarbon chain, the $\text{C}_{17}\text{H}_{35}$ — unit, and an ionic carboxylate group, the —CO_2^- unit ([\[link\]](#)).



Soaps contain a nonpolar hydrocarbon end (blue) and an ionic end (red). The ionic end is a carboxylate group. The length of the hydrocarbon end can vary from soap to soap.

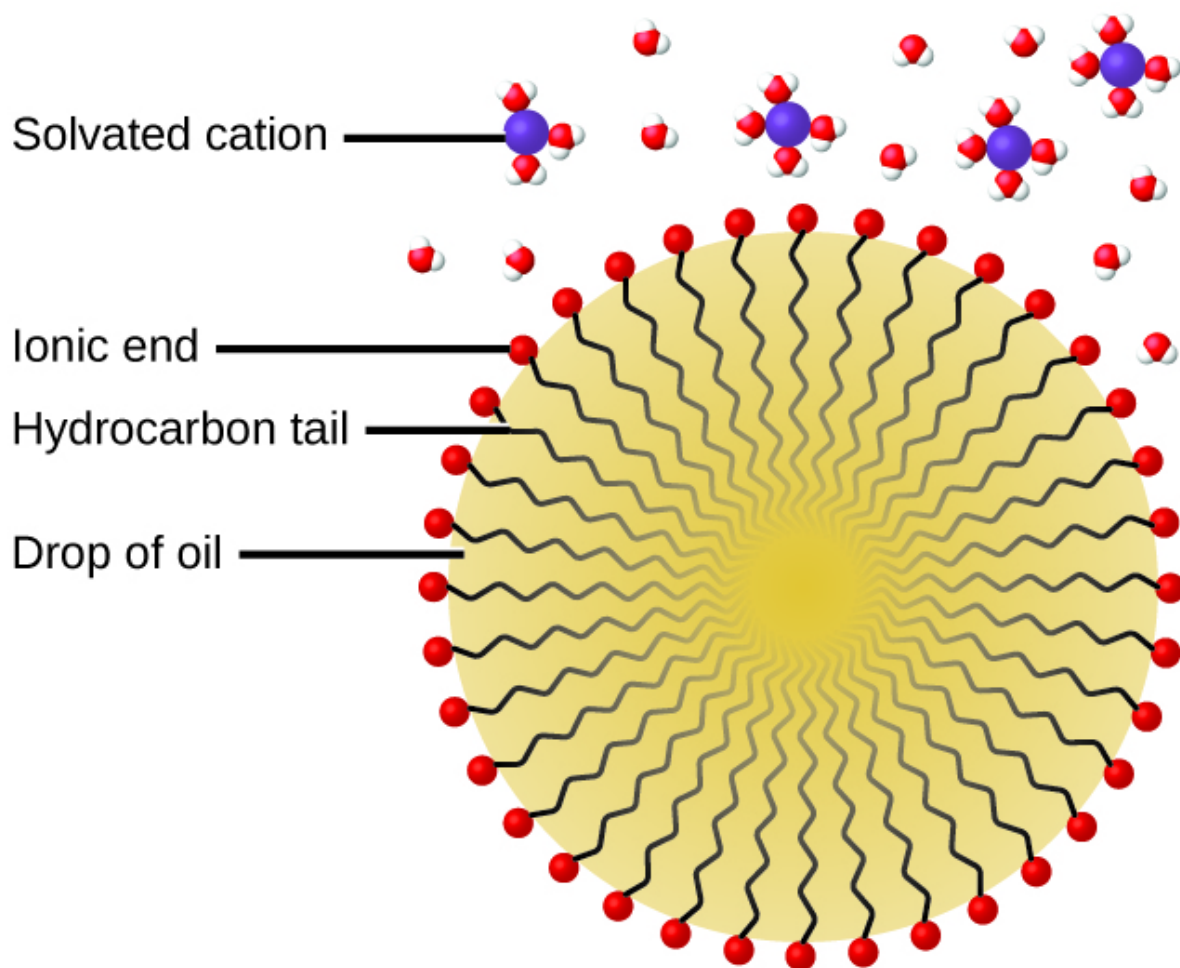
Detergents (soap substitutes) also contain nonpolar hydrocarbon chains, such as $\text{C}_{12}\text{H}_{25}$ —, and an ionic group, such as a sulfate— OSO_3^- , or a sulfonate— SO_3^- ([\[link\]](#)). Soaps form insoluble calcium and magnesium compounds in hard water; detergents form water-soluble products—a definite advantage for detergents.



Detergents contain a nonpolar hydrocarbon end (blue) and an ionic end (red). The ionic end can be either a sulfate or a sulfonate. The length of the hydrocarbon end can vary from detergent to detergent.

The cleaning action of soaps and detergents can be explained in terms of the structures of the molecules involved. The hydrocarbon (nonpolar) end of a soap or detergent molecule dissolves in, or is attracted to, nonpolar substances such as oil, grease, or dirt particles. The ionic end is attracted by water (polar), illustrated in [\[link\]](#). As a result, the soap or detergent molecules become oriented at the interface between the dirt particles and the water so they act as a kind of bridge between two different kinds of matter, nonpolar and polar. Molecules such as this are termed **amphiphilic** since they have both a hydrophobic (“water-fearing”)

part and a hydrophilic (“water-loving”) part. As a consequence, dirt particles become suspended as colloidal particles and are readily washed away.



This diagrammatic cross section of an emulsified drop of oil in water shows how soap or detergent acts as an emulsifier.

Note:

Deepwater Horizon Oil Spill

The blowout of the Deepwater Horizon oil drilling rig on April 20, 2010, in the Gulf of Mexico near Mississippi began the largest marine oil spill in the history

of the petroleum industry. In the 87 days following the blowout, an estimated 4.9 million barrels (210 million gallons) of oil flowed from the ruptured well 5000 feet below the water's surface. The well was finally declared sealed on September 19, 2010.

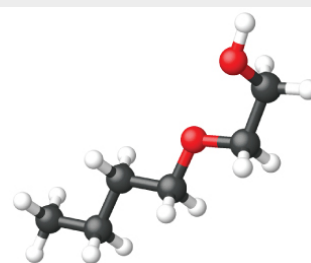
Crude oil is immiscible with and less dense than water, so the spilled oil rose to the surface of the water. Floating booms, skimmer ships, and controlled burns were used to remove oil from the water's surface in an attempt to protect beaches and wetlands along the Gulf coast. In addition to removal of the oil, attempts were also made to lessen its environmental impact by rendering it "soluble" (in the loose sense of the term) and thus allowing it to be diluted to hopefully less harmful levels by the vast volume of ocean water. This approach used 1.84 million gallons of the oil dispersant Corexit 9527, most of which was injected underwater at the site of the leak, with small amounts being sprayed on top of the spill. Corexit 9527 contains 2-butoxyethanol ($C_6H_{14}O_2$), an amphiphilic molecule whose polar and nonpolar ends are useful for emulsifying oil into small droplets, increasing the surface area of the oil and making it more available to marine bacteria for digestion ([\[link\]](#)). While this approach avoids many of the immediate hazards that bulk oil poses to marine and coastal ecosystems, it introduces the possibility of long-term effects resulting from the introduction of the complex and potential toxic components of petroleum into the ocean's food chain. A number of organizations are involved in monitoring the extended impact of this oil spill, including the National Oceanic and Atmospheric Administration (visit this [website](#) for additional details).



(a)



(b)



(c)

(a) This NASA satellite image shows the oil slick from the Deepwater Horizon spill. (b) A US Air Force plane sprays Corexit, a dispersant. (c)

The molecular structure of 2-butoxyethanol is shown. (credit a: modification of work by "NASA, FT2, demis.nl"/Wikimedia Commons; credit b: modification of work by "NASA/MODIS Rapid Response Team"/Wikimedia Commons)

Electrical Properties of Colloidal Particles

Dispersed colloidal particles are often electrically charged. A colloidal particle of iron(III) hydroxide, for example, does not contain enough hydroxide ions to compensate exactly for the positive charges on the iron(III) ions. Thus, each individual colloidal particle bears a positive charge, and the colloidal dispersion consists of charged colloidal particles and some free hydroxide ions, which keep the dispersion electrically neutral. Most metal hydroxide colloids have positive charges, whereas most metals and metal sulfides form negatively charged dispersions. All colloidal particles in any one system have charges of the same sign. This helps keep them dispersed because particles containing like charges repel each other.

We can take advantage of the charge on colloidal particles to remove them from a variety of mixtures. If we place a colloidal dispersion in a container with charged electrodes, positively charged particles, such as iron(III) hydroxide particles, would move to the negative electrode. There, the colloidal particles lose their charge and coagulate as a precipitate.

The carbon and dust particles in smoke are often colloiddally dispersed and electrically charged. Frederick Cottrell, an American chemist, developed a process to remove these particles.

Note:

Frederick Gardner Cottrell



(a)

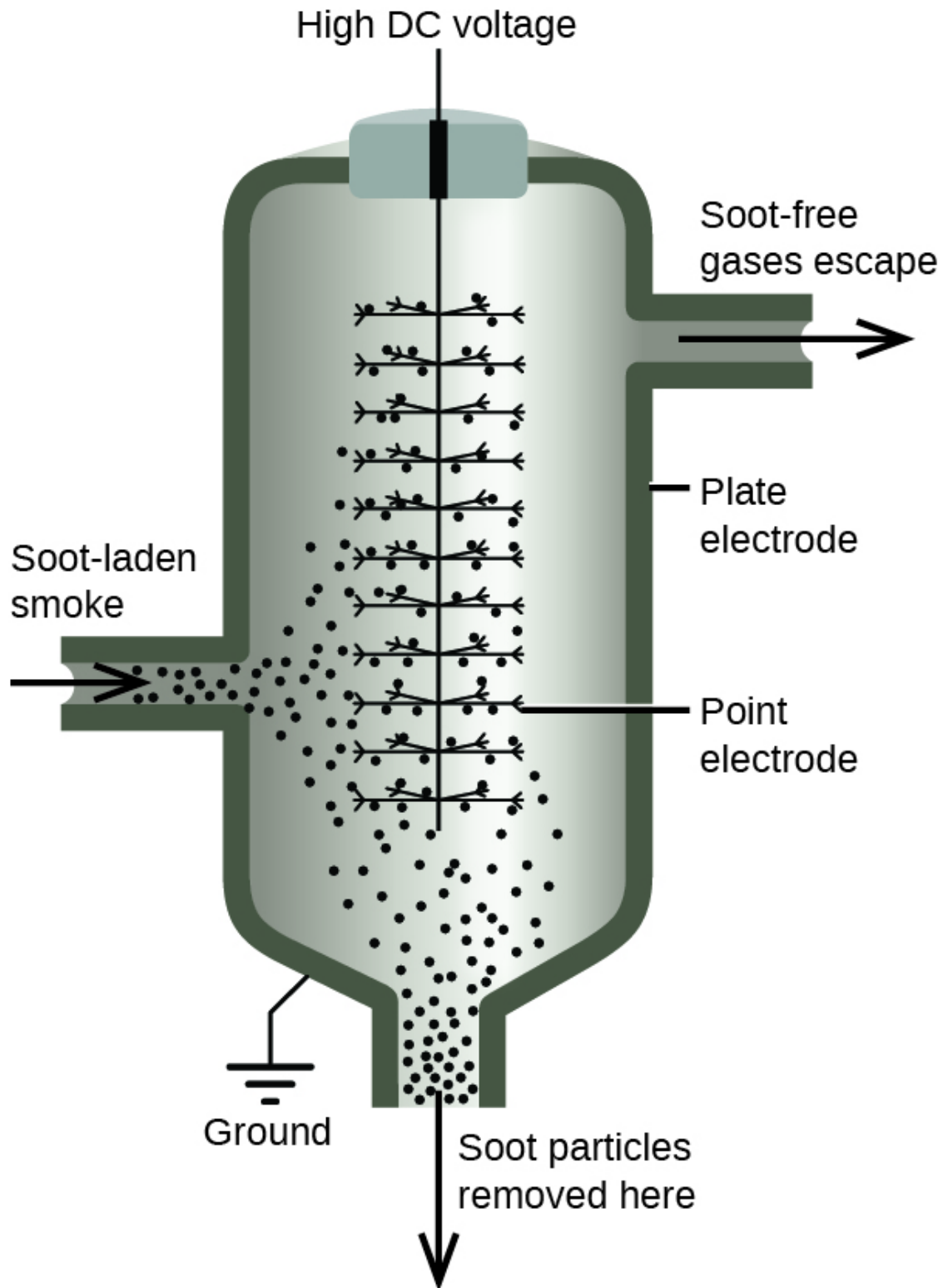


(b)

(a) Frederick Cottrell developed (b) the electrostatic precipitator, a device designed to curb air pollution by removing colloidal particles from air. (credit b: modification of work by “SpLot”/Wikimedia Commons)

Born in Oakland, CA in 1877, Frederick Cottrell devoured textbooks as if they were novels and graduated from high school at the age of 16. He then entered the University of California (UC), Berkeley, completing a Bachelor's degree in three years. He saved money from his \$1200 annual salary as a chemistry teacher at Oakland High School to fund his studies in chemistry in Berlin with Nobel prize winner Jacobus Henricus van't Hoff, and in Leipzig with Wilhelm Ostwald, another Nobel awardee. After earning his PhD in physical chemistry, he returned to the United States to teach at UC Berkeley. He also consulted for the DuPont Company, where he developed the electrostatic precipitator, a device designed to curb air pollution by removing colloidal particles from air. Cottrell used the proceeds from his invention to fund a nonprofit research corporation to finance scientific research.

The charged particles are attracted to highly charged electrodes, where they are neutralized and deposited as dust ([link](#)). This is one of the important methods used to clean up the smoke from a variety of industrial processes. The process is also important in the recovery of valuable products from the smoke and flue dust of smelters, furnaces, and kilns. There are also ionic air filters designed for home use to improve indoor air quality.

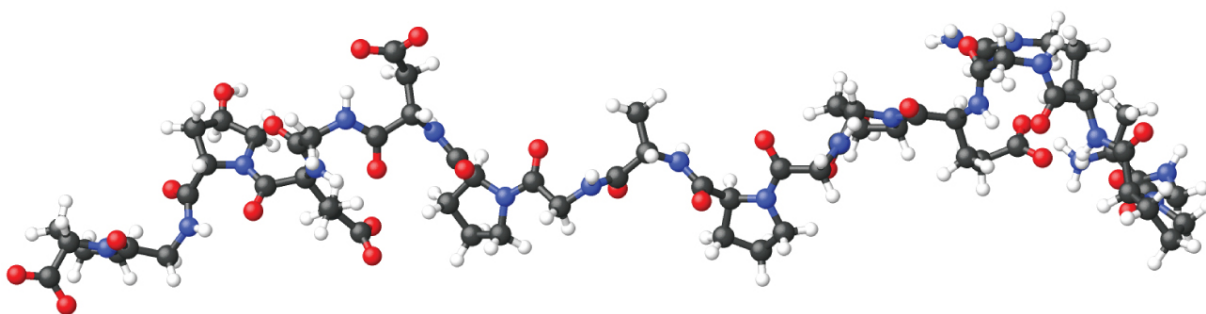


In a Cottrell precipitator, positively and negatively charged particles are attracted to highly charged electrodes, where they are neutralized and

deposited as dust.

Gels

When we make gelatin, such as Jell-O, we are making a type of colloid ([\[link\]](#)). Gelatin sets on cooling because the hot aqueous mixture of gelatin coagulates as it cools and the whole mass, including the liquid, sets to an extremely viscous body known as a **gel**, a colloid in which the dispersing medium is a solid and the dispersed phase is a liquid. It appears that the fibers of the dispersing medium form a complex three-dimensional network, the interstices being filled with the liquid medium or a dilute solution of the dispersing medium. Because the formation of a gel is accompanied by the taking up of water or some other solvent, the gel is said to be hydrated or solvated.



Gelatin desserts are colloids in which an aqueous solution of sweeteners and flavors is dispersed throughout a medium of solid proteins. (credit photo: modification of work by Steven Depolo)

Pectin, a carbohydrate from fruit juices, is a gel-forming substance important in jelly making. Silica gel, a colloidal dispersion of hydrated silicon dioxide, is formed when dilute hydrochloric acid is added to a dilute solution of sodium silicate. Canned Heat is a gel made by mixing alcohol and a saturated aqueous solution of calcium acetate.

Key Concepts and Summary

Colloids are mixtures in which one or more substances are dispersed as relatively large solid particles or liquid droplets throughout a solid, liquid, or gaseous medium. The particles of a colloid remain dispersed and do not settle due to gravity, and they are often electrically charged. Colloids are widespread in nature and are involved in many technological applications.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Identify the dispersed phase and the dispersion medium in each of the following colloidal systems: starch dispersion, smoke, fog, pearl, whipped cream, floating soap, jelly, milk, and ruby.

Solution:

Colloidal System	Dispersed Phase	Dispersion Medium
starch dispersion	starch	water
smoke	solid particles	air

Colloidal System	Dispersed Phase	Dispersion Medium
fog	water	air
pearl	water	calcium carbonate (CaCO ₃)
whipped cream	air	cream
floating soap	air	soap
jelly	fruit juice	pectin gel
milk	butterfat	water
ruby	chromium(III) oxide (Cr ₂ O ₃)	aluminum oxide (Al ₂ O ₃)

Exercise:

Problem:

Distinguish between dispersion methods and condensation methods for preparing colloidal systems.

Exercise:

Problem:

How do colloids differ from solutions with regard to dispersed particle size and homogeneity?

Solution:

Colloidal dispersions consist of particles that are much bigger than the solutes of typical solutions. Colloidal particles are either very large molecules or aggregates of smaller species that usually are big enough to scatter light. Colloids are homogeneous on a macroscopic (visual) scale, while solutions are homogeneous on a microscopic (molecular) scale.

Exercise:

Problem: Explain the cleansing action of soap.

Exercise:

Problem:

How can it be demonstrated that colloidal particles are electrically charged?

Solution:

If they are placed in an electrolytic cell, dispersed particles will move toward the electrode that carries a charge opposite to their own charge. At this electrode, the charged particles will be neutralized and will coagulate as a precipitate.

Glossary

amphiphilic

molecules possessing both hydrophobic (nonpolar) and a hydrophilic (polar) parts

colloid

(also, colloidal dispersion) mixture in which relatively large solid or liquid particles are dispersed uniformly throughout a gas, liquid, or solid

dispersion medium

solid, liquid, or gas in which colloidal particles are dispersed

dispersed phase

substance present as relatively large solid or liquid particles in a colloid

emulsifying agent

amphiphilic substance used to stabilize the particles of some emulsions

emulsion

colloid formed from immiscible liquids

gel

colloidal dispersion of a liquid in a solid

Tyndall effect
scattering of visible light by a colloidal dispersion

Precipitation and Dissolution

By the end of this section, you will be able to:

- Write chemical equations and equilibrium expressions representing solubility equilibria
- Carry out equilibrium computations involving solubility, equilibrium expressions, and solute concentrations

The preservation of medical laboratory blood samples, mining of sea water for magnesium, formulation of over-the-counter medicines such as Milk of Magnesia and antacids, and treating the presence of hard water in your home's water supply are just a few of the many tasks that involve controlling the equilibrium between a slightly soluble ionic solid and an aqueous solution of its ions.

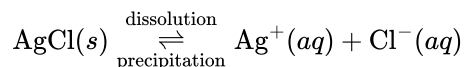
In some cases, we want to prevent dissolution from occurring. Tooth decay, for example, occurs when the calcium hydroxylapatite, which has the formula $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, in our teeth dissolves. The dissolution process is aided when bacteria in our mouths feast on the sugars in our diets to produce lactic acid, which reacts with the hydroxide ions in the calcium hydroxylapatite. Preventing the dissolution prevents the decay. On the other hand, sometimes we want a substance to dissolve. We want the calcium carbonate in a chewable antacid to dissolve because the CO_3^{2-} ions produced in this process help soothe an upset stomach.

In this section, we will find out how we can control the dissolution of a slightly soluble ionic solid by the application of Le Châtelier's principle. We will also learn how to use the equilibrium constant of the reaction to determine the concentration of ions present in a saturated solution.

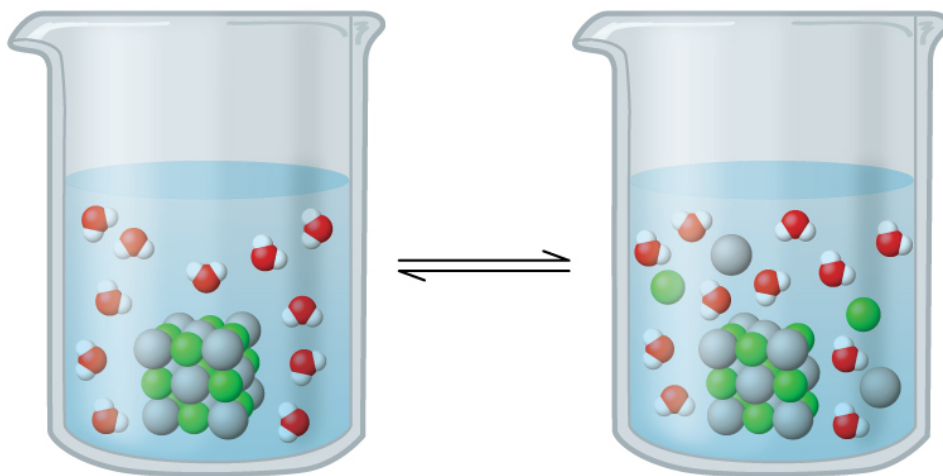
The Solubility Product

Silver chloride is what's known as a sparingly soluble ionic solid ([link](#)). Recall from the solubility rules in an earlier chapter that halides of Ag^+ are not normally soluble. However, when we add an excess of solid AgCl to water, it dissolves to a small extent and produces a mixture consisting of a very dilute solution of Ag^+ and Cl^- ions in equilibrium with undissolved silver chloride:

Equation:



This equilibrium, like other equilibria, is dynamic; some of the solid AgCl continues to dissolve, but at the same time, Ag^+ and Cl^- ions in the solution combine to produce an equal amount of the solid. At equilibrium, the opposing processes have equal rates.



Silver chloride is a sparingly soluble ionic solid. When it is added to water, it dissolves slightly and produces a mixture consisting of a very dilute solution of Ag^+ and Cl^- ions in equilibrium with undissolved silver chloride.

The equilibrium constant for the equilibrium between a slightly soluble ionic solid and a solution of its ions is called the **solubility product (K_{sp})** of the solid. Recall from the chapter on solutions and colloids that we use an ion's concentration as an approximation of its activity in a dilute solution. For silver chloride, at equilibrium:

Equation:



Note that the K_{sp} expression does not contain a term in the denominator for the concentration of the reactant, AgCl . According to the guidelines for deriving mass-action expressions described in an earlier chapter on equilibrium, only gases and solutes are represented. Solids and liquids are assigned concentration values of one and thus do not appear in equilibrium constant expressions; therefore, $[\text{AgCl}]$ does not appear in the expression for K_{sp} .

Some common solubility products are listed in [\[link\]](#) according to their K_{sp} values, whereas a more extensive compilation of solubility products appears in [Appendix J](#). Each of these equilibrium constants is much smaller than 1 because the compounds listed are only slightly soluble. A small K_{sp} represents a system in which the equilibrium lies to the left, so that relatively few hydrated ions would be present in a saturated solution.

Common Solubility Products by Decreasing Equilibrium Constants	
Substance	K_{sp} at 25 °C
CuCl	1.2×10^{-6}
CuBr	6.27×10^{-9}
AgI	1.5×10^{-16}
PbS	7×10^{-29}
$\text{Al}(\text{OH})_3$	2×10^{-32}
$\text{Fe}(\text{OH})_3$	4×10^{-38}

Example:

Writing Equations and Solubility Products

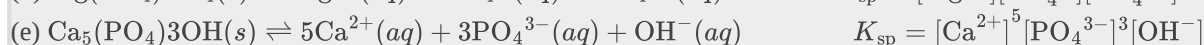
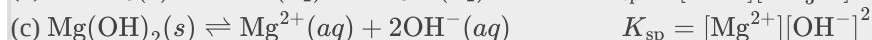
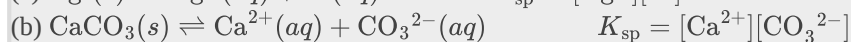
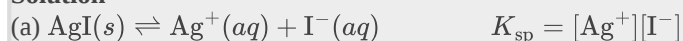
Write the ionic equation for the dissolution and the solubility product expression for each of the following slightly soluble ionic compounds:

- AgI, silver iodide, a solid with antiseptic properties
- CaCO_3 , calcium carbonate, the active ingredient in many over-the-counter chewable antacids
- $\text{Mg}(\text{OH})_2$, magnesium hydroxide, the active ingredient in Milk of Magnesia
- $\text{Mg}(\text{NH}_4)\text{PO}_4$, magnesium ammonium phosphate, an essentially insoluble substance used in tests for magnesium

(e) $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, the mineral apatite, a source of phosphate for fertilizers

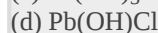
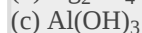
(Hint: When determining how to break (d) and (e) up into ions, refer to the list of polyatomic ions in the section on chemical nomenclature.)

Solution



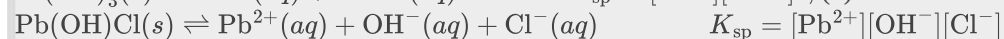
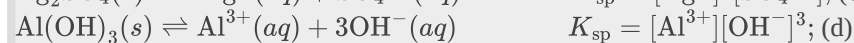
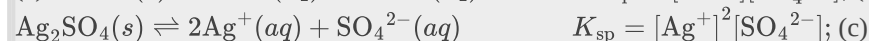
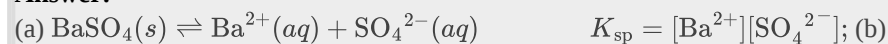
Check Your Learning

Write the ionic equation for the dissolution and the solubility product for each of the following slightly soluble compounds:



Note:

Answer:

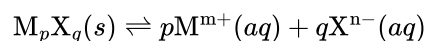


Now we will extend the discussion of K_{sp} and show how the solubility product is determined from the solubility of its ions, as well as how K_{sp} can be used to determine the molar solubility of a substance.

K_{sp} and Solubility

The K_{sp} of a slightly soluble ionic compound may be simply related to its measured solubility provided the dissolution process involves only dissociation and solvation, for example:

Equation:



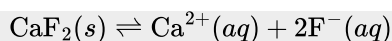
For cases such as these, one may derive K_{sp} values from provided solubilities, or vice-versa. Calculations of this sort are most conveniently performed using a compound's molar solubility, measured as moles of dissolved solute per liter of saturated solution.

Example:

Calculation of K_{sp} from Equilibrium Concentrations

We began the chapter with an informal discussion of how the mineral fluorite ([link](#)) is formed. Fluorite, CaF_2 , is a slightly soluble solid that dissolves according to the equation:

Equation:

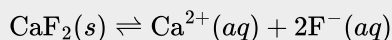


The concentration of Ca^{2+} in a saturated solution of CaF_2 is $2.15 \times 10^{-4} M$; therefore, that of F^{-} is $4.30 \times 10^{-4} M$, that is, twice the concentration of Ca^{2+} . What is the solubility product of fluorite?

Solution

First, write out the K_{sp} expression, then substitute in concentrations and solve for K_{sp} :

Equation:



A saturated solution is a solution at equilibrium with the solid. Thus:

Equation:

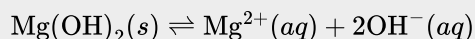
$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{F}^{-}]^2 = (2.15 \times 10^{-4})(4.30 \times 10^{-4})^2 = 3.98 \times 10^{-11}$$

As with other equilibrium constants, we do not include units with K_{sp} .

Check Your Learning

In a saturated solution that is in contact with solid $\text{Mg}(\text{OH})_2$, the concentration of Mg^{2+} is $1.31 \times 10^{-4} M$. What is the solubility product for $\text{Mg}(\text{OH})_2$?

Equation:



Note:

Answer:

$$8.99 \times 10^{-12}$$

Example:

Determination of Molar Solubility from K_{sp}

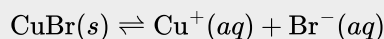
The K_{sp} of copper(I) bromide, CuBr , is 6.3×10^{-9} . Calculate the molar solubility of copper bromide.

Solution

The solubility product of copper(I) bromide is 6.3×10^{-9} .

The reaction is:

Equation:



First, write out the solubility product expression:

Equation:

$$K_{\text{sp}} = [\text{Cu}^{+}][\text{Br}^{-}]$$

Create an ICE table (as introduced in the chapter on fundamental equilibrium concepts), leaving the CuBr column empty as it is a solid and does not contribute to the K_{sp} :

	$\text{CuBr (s)} \rightleftharpoons \text{Cu}^+ (\text{aq}) + \text{Br}^- (\text{aq})$		
Initial concentration (M)		0	0
Change (M)		x	x
Equilibrium concentration (M)		$0 + x = x$	$0 + x = x$

At equilibrium:

Equation:

$$K_{\text{sp}} = [\text{Cu}^+][\text{Br}^-]$$

Equation:

$$6.3 \times 10^{-9} = (x)(x) = x^2$$

Equation:

$$x = \sqrt{(6.3 \times 10^{-9})} = 7.9 \times 10^{-5}$$

Therefore, the molar solubility of CuBr is $7.9 \times 10^{-5} M$.

Check Your Learning

The K_{sp} of AgI is 1.5×10^{-16} . Calculate the molar solubility of silver iodide.

Note:

Answer:

$$1.2 \times 10^{-8} M$$

Example:

Determination of Molar Solubility from K_{sp} , Part II

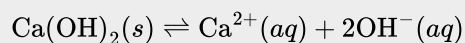
The K_{sp} of calcium hydroxide, Ca(OH)_2 , is 1.3×10^{-6} . Calculate the molar solubility of calcium hydroxide.

Solution

The solubility product of calcium hydroxide is 1.3×10^{-6} .

The reaction is:

Equation:



First, write out the solubility product expression:

Equation:

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{OH}^-]^2$$

Create an ICE table, leaving the Ca(OH)_2 column empty as it is a solid and does not contribute to the K_{sp} :

	$\text{Ca(OH)}_2 (\text{s}) \rightleftharpoons \text{Ca}^{2+} (\text{aq}) + 2\text{OH}^- (\text{aq})$		
Initial concentration (M)		0	0
Change (M)		x	$2x$
Equilibrium concentration (M)		$0 + x = x$	$0 + 2x = 2x$

At equilibrium:

Equation:

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{OH}^-]^2$$

Equation:

$$1.3 \times 10^{-6} = (x)(2x)^2 = (x)(4x^2) = 4x^3$$

Equation:

$$x = \sqrt[3]{\frac{1.3 \times 10^{-6}}{4}} = 6.9 \times 10^{-3}$$

Therefore, the molar solubility of Ca(OH)_2 is $6.9 \times 10^{-3} \text{ M}$.

Check Your Learning

The K_{sp} of PbI_2 is 1.4×10^{-8} . Calculate the molar solubility of lead(II) iodide.

Note:

Answer:

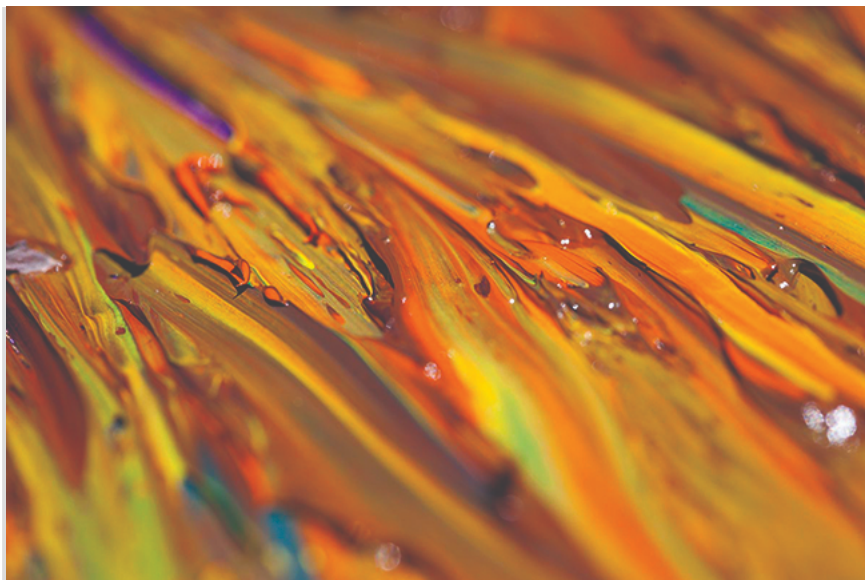
$$1.5 \times 10^{-3} \text{ M}$$

Note that solubility is not always given as a molar value. When the solubility of a compound is given in some unit other than moles per liter, we must convert the solubility into moles per liter (i.e., molarity) in order to use it in the solubility product expression. [\[link\]](#) shows how to perform those unit conversions before determining the solubility product equilibrium.

Example:

Determination of K_{sp} from Gram Solubility

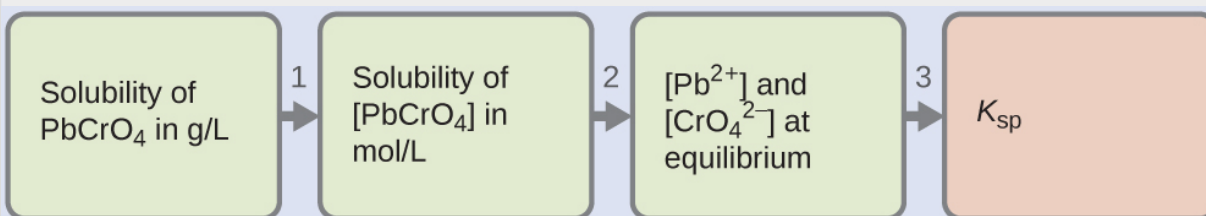
Many of the pigments used by artists in oil-based paints ([\[link\]](#)) are sparingly soluble in water. For example, the solubility of the artist's pigment chrome yellow, PbCrO_4 , is $4.6 \times 10^{-6} \text{ g/L}$. Determine the solubility product for PbCrO_4 .



Oil paints contain pigments that are very slightly soluble in water. In addition to chrome yellow (PbCrO_4), examples include Prussian blue ($\text{Fe}_7(\text{CN})_{18}$), the reddish-orange color vermilion (HgS), and green color veridian (Cr_2O_3). (credit: Sonny Abesamis)

Solution

We are given the solubility of PbCrO_4 in grams per liter. If we convert this solubility into moles per liter, we can find the equilibrium concentrations of Pb^{2+} and CrO_4^{2-} , then K_{sp} :



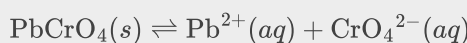
Equation:

Use the molar mass of PbCrO_4 $\left(\frac{323.2 \text{ g}}{1 \text{ mol}}\right)$ to convert the solubility of PbCrO_4 in grams per liter into moles per liter:

$$\begin{aligned}
 [\text{PbCrO}_4] &= \frac{4.6 \times 10^{-6} \text{ g PbCrO}_4}{1 \text{ L}} \times \frac{1 \text{ mol PbCrO}_4}{323.2 \text{ g PbCrO}_4} \\
 &= \frac{1.4 \times 10^{-8} \text{ mol PbCrO}_4}{1 \text{ L}} \\
 &= 1.4 \times 10^{-8} M
 \end{aligned}$$

Equation:

The chemical equation for the dissolution indicates that 1 mol of PbCrO_4 gives 1 mol of Pb^{2+}



Thus, both $[\text{Pb}^{2+}]$ and $[\text{CrO}_4^{2-}]$ are equal to the molar solubility of PbCrO_4 :

Equation:

$$[\text{Pb}^{2+}] = [\text{CrO}_4^{2-}] = 1.4 \times 10^{-8} M$$

(aq) and 1 mol of $\text{CrO}_4^{2-}(\text{aq})$:

Solve. $K_{\text{sp}} = [\text{Pb}^{2+}][\text{CrO}_4^{2-}] = (1.4 \times 10^{-8})(1.4 \times 10^{-8}) = 2.0 \times 10^{-16}$

Check Your Learning

The solubility of TlCl [thallium(I) chloride], an intermediate formed when thallium is being isolated from ores, is 3.46 grams per liter at 20 °C. What is its solubility product?

Note:

Answer:

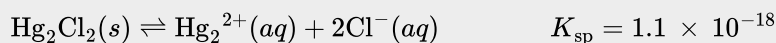
2.08×10^{-4}

Example:

Calculating the Solubility of Hg_2Cl_2

Calomel, Hg_2Cl_2 , is a compound composed of the diatomic ion of mercury(I), Hg_2^{2+} , and chloride ions, Cl^- . Although most mercury compounds are now known to be poisonous, eighteenth-century physicians used calomel as a medication. Their patients rarely suffered any mercury poisoning from the treatments because calomel is quite insoluble:

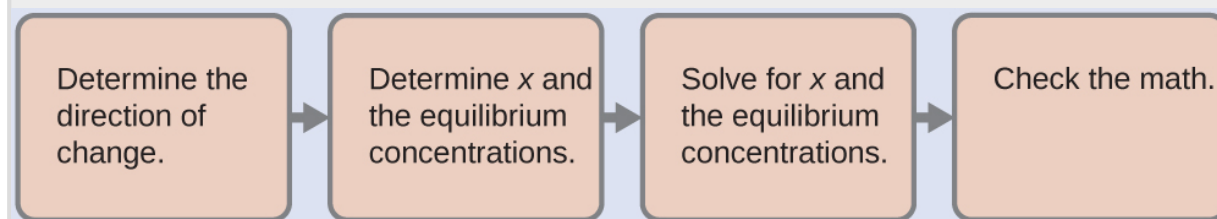
Equation:



Calculate the molar solubility of Hg_2Cl_2 .

Solution

The molar solubility of Hg_2Cl_2 is equal to the concentration of Hg_2^{2+} ions because for each 1 mol of Hg_2Cl_2 that dissolves, 1 mol of Hg_2^{2+} forms:



Determine the direction of change. Before any Hg_2Cl_2 dissolves, Q is zero, and the reaction will shift to the right to reach equilibrium.

Determine x and equilibrium concentrations.

Concentrations and changes are given in the following ICE table:

	$\text{Hg}_2\text{Cl}_2(\text{s}) \rightleftharpoons \text{Hg}_2^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq})$	
Initial concentration (M)	0	0
Change (M)	x	2x
Equilibrium concentration (M)	0 + x = x	0 + 2x = 2x

Note that the change in the concentration of Cl^- ($2x$) is twice as large as the change in the concentration of Hg_2^{2+} (x) because 2 mol of Cl^- forms for each 1 mol of Hg_2^{2+} that forms. Hg_2Cl_2 is a pure solid, so it does not appear in the calculation.

Equation:

Equation:

Equation:

Equation:

Solve for x and

the equilibrium concentrations. $K_{\text{sp}} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 = 1.1 \times 10^{-18} = (x)(2x)^2 = 4x^3 = 1.1 \times 10^{-18}$

We substitute the equilibrium concentrations into the expression for K_{sp} and calculate the value of x :

$$x = \sqrt[3]{\left(\frac{1.1 \times 10^{-18}}{4}\right)} =$$

Equation:

Check the work. At equilibrium, $Q = K_{sp}$:

$$Q = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 = (6.5 \times 10^{-7})(1.3 \times 10^{-6})^2 = 1.1 \times 10^{-18}$$

The calculations check.

Check Your Learning

Determine the molar solubility of MgF_2 from its solubility product: $K_{sp} = 6.4 \times 10^{-9}$.

Note:

Answer:

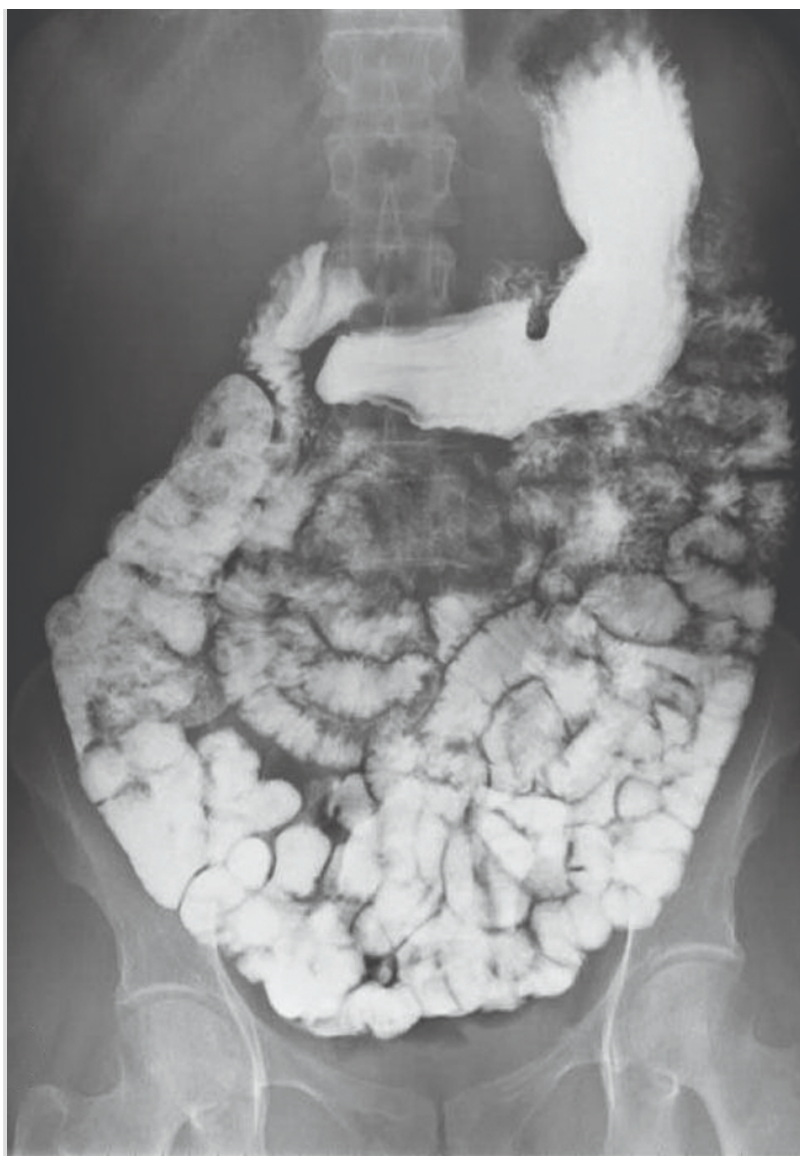
$$1.2 \times 10^{-3} M$$

Tabulated K_{sp} values can also be compared to reaction quotients calculated from experimental data to tell whether a solid will precipitate in a reaction under specific conditions: Q equals K_{sp} at equilibrium; if Q is less than K_{sp} , the solid will dissolve until Q equals K_{sp} ; if Q is greater than K_{sp} , precipitation will occur at a given temperature until Q equals K_{sp} .

Note:

Using Barium Sulfate for Medical Imaging

Various types of medical imaging techniques are used to aid diagnoses of illnesses in a noninvasive manner. One such technique utilizes the ingestion of a barium compound before taking an X-ray image. A suspension of barium sulfate, a chalky powder, is ingested by the patient. Since the K_{sp} of barium sulfate is 1.1×10^{-10} , very little of it dissolves as it coats the lining of the patient's intestinal tract. Barium-coated areas of the digestive tract then appear on an X-ray as white, allowing for greater visual detail than a traditional X-ray ([link](#)).



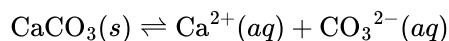
The suspension of barium sulfate coats the intestinal tract, which allows for greater visual detail than a traditional X-ray. (credit modification of work by “glitzy queen00”/Wikimedia Commons)

Further diagnostic testing can be done using barium sulfate and fluoroscopy. In fluoroscopy, a continuous X-ray is passed through the body so the doctor can monitor, on a TV or computer screen, the barium sulfate's movement as it passes through the digestive tract. Medical imaging using barium sulfate can be used to diagnose acid reflux disease, Crohn's disease, and ulcers in addition to other conditions.

Visit this [website](#) for more information on how barium is used in medical diagnoses and which conditions it is used to diagnose.

Predicting Precipitation

The equation that describes the equilibrium between solid calcium carbonate and its solvated ions is:

Equation:

We can establish this equilibrium either by adding solid calcium carbonate to water or by mixing a solution that contains calcium ions with a solution that contains carbonate ions. If we add calcium carbonate to water, the solid will dissolve until the concentrations are such that the value of the reaction quotient ($Q = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$) is equal to the solubility product ($K_{\text{sp}} = 8.7 \times 10^{-9}$). If we mix a solution of calcium nitrate, which contains Ca^{2+} ions, with a solution of sodium carbonate, which contains CO_3^{2-} ions, the slightly soluble ionic solid CaCO_3 will precipitate, provided that the concentrations of Ca^{2+} and CO_3^{2-} ions are such that Q is greater than K_{sp} for the mixture. The reaction shifts to the left and the concentrations of the ions are reduced by formation of the solid until the value of Q equals K_{sp} . A saturated solution in equilibrium with the undissolved solid will result. If the concentrations are such that Q is less than K_{sp} , then the solution is not saturated and no precipitate will form.

We can compare numerical values of Q with K_{sp} to predict whether precipitation will occur, as [\[link\]](#) shows. (Note: Since all forms of equilibrium constants are temperature dependent, we will assume a room temperature environment going forward in this chapter unless a different temperature value is explicitly specified.)

Example:**Precipitation of $\text{Mg}(\text{OH})_2$**

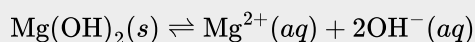
The first step in the preparation of magnesium metal is the precipitation of $\text{Mg}(\text{OH})_2$ from sea water by the addition of lime, $\text{Ca}(\text{OH})_2$, a readily available inexpensive source of OH^- ion:

Equation:

The concentration of $\text{Mg}^{2+}(aq)$ in sea water is 0.0537 M . Will $\text{Mg}(\text{OH})_2$ precipitate when enough $\text{Ca}(\text{OH})_2$ is added to give a $[\text{OH}^-]$ of 0.0010 M ?

Solution

This problem asks whether the reaction:

Equation:

shifts to the left and forms solid $\text{Mg}(\text{OH})_2$ when $[\text{Mg}^{2+}] = 0.0537 \text{ M}$ and $[\text{OH}^-] = 0.0010 \text{ M}$. The reaction shifts to the left if Q is greater than K_{sp} . Calculation of the reaction quotient under these conditions is shown here:

Equation:

$$Q = [\text{Mg}^{2+}][\text{OH}^-]^2 = (0.0537)(0.0010)^2 = 5.4 \times 10^{-8}$$

Because Q is greater than K_{sp} ($Q = 5.4 \times 10^{-8}$ is larger than $K_{\text{sp}} = 8.9 \times 10^{-12}$), we can expect the reaction to shift to the left and form solid magnesium hydroxide. $\text{Mg}(\text{OH})_2(s)$ forms until the concentrations of magnesium ion and hydroxide ion are reduced sufficiently so that the value of Q is equal to K_{sp} .

Check Your Learning

Use the solubility product in [Appendix J](#) to determine whether CaHPO_4 will precipitate from a solution with $[\text{Ca}^{2+}] = 0.0001 \text{ M}$ and $[\text{HPO}_4^{2-}] = 0.001 \text{ M}$.

Note:**Answer:**

No precipitation of CaHPO_4 ; $Q = 1 \times 10^{-7}$, which is less than K_{sp}

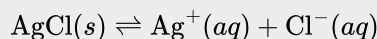
Example:**Precipitation of AgCl upon Mixing Solutions**

Does silver chloride precipitate when equal volumes of a $2.0 \times 10^{-4}\text{-}M$ solution of AgNO_3 and a $2.0 \times 10^{-4}\text{-}M$ solution of NaCl are mixed?

(Note: The solution also contains Na^+ and NO_3^- ions, but when referring to solubility rules, one can see that sodium nitrate is very soluble and cannot form a precipitate.)

Solution

The equation for the equilibrium between solid silver chloride, silver ion, and chloride ion is:

Equation:

The solubility product is 1.6×10^{-10} (see [Appendix J](#)).

AgCl will precipitate if the reaction quotient calculated from the concentrations in the mixture of AgNO_3 and NaCl is greater than K_{sp} . The volume doubles when we mix equal volumes of AgNO_3 and NaCl solutions, so each concentration is reduced to half its initial value. Consequently, immediately upon mixing, $[\text{Ag}^+]$ and $[\text{Cl}^-]$ are both equal to:

Equation:

$$\frac{1}{2}(2.0 \times 10^{-4})\text{ }M = 1.0 \times 10^{-4}\text{ }M$$

The reaction quotient, Q , is *momentarily* greater than K_{sp} for AgCl , so a supersaturated solution is formed:

Equation:

$$Q = [\text{Ag}^+][\text{Cl}^-] = (1.0 \times 10^{-4})(1.0 \times 10^{-4}) = 1.0 \times 10^{-8} > K_{\text{sp}}$$

Since supersaturated solutions are unstable, AgCl will precipitate from the mixture until the solution returns to equilibrium, with Q equal to K_{sp} .

Check Your Learning

Will KClO_4 precipitate when 20 mL of a $0.050\text{-}M$ solution of K^+ is added to 80 mL of a $0.50\text{-}M$ solution of ClO_4^- ? (Remember to calculate the new concentration of each ion after mixing the solutions before plugging into the reaction quotient expression.)

Note:**Answer:**

No, $Q = 4.0 \times 10^{-3}$, which is less than $K_{\text{sp}} = 1.05 \times 10^{-2}$

In the previous two examples, we have seen that $\text{Mg}(\text{OH})_2$ or AgCl precipitate when Q is greater than K_{sp} . In general, when a solution of a soluble salt of the M^{m+} ion is mixed with a solution of a soluble salt of the X^{n-} ion, the solid, M_pX_q precipitates if the value of Q for the mixture of M^{m+} and X^{n-} is greater than K_{sp} for M_pX_q . Thus, if we know the concentration of one of the ions of a slightly soluble ionic solid and the value for the solubility product of the solid, then we can calculate the concentration that the other ion must exceed for precipitation to begin. To simplify the calculation, we will assume that precipitation begins when the reaction quotient becomes equal to the solubility product.

Example:**Precipitation of Calcium Oxalate**

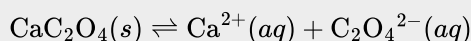
Blood will not clot if calcium ions are removed from its plasma. Some blood collection tubes contain salts of the oxalate ion, $\text{C}_2\text{O}_4^{2-}$, for this purpose ([link](#)). At sufficiently high concentrations, the calcium and oxalate ions form solid, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (which also contains water bound in the solid). The concentration of Ca^{2+} in a sample of blood serum is $2.2 \times 10^{-3} \text{ M}$. What concentration of $\text{C}_2\text{O}_4^{2-}$ ion must be established before $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ begins to precipitate?



Anticoagulants can be added to blood that will combine with the Ca^{2+} ions in blood serum and prevent the blood from clotting.
(credit: modification of work by Neeta Lind)

Solution

The equilibrium expression is:

Equation:

For this reaction:

Equation:

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = 1.96 \times 10^{-8}$$

(see [Appendix J](#))

CaC_2O_4 does not appear in this expression because it is a solid. Water does not appear because it is the solvent. Solid CaC_2O_4 does not begin to form until Q equals K_{sp} . Because we know K_{sp} and $[\text{Ca}^{2+}]$, we can solve for the concentration of $\text{C}_2\text{O}_4^{2-}$ that is necessary to produce the first trace of solid:

Equation:

$$Q = K_{\text{sp}} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = 1.96 \times 10^{-8}$$

Equation:

$$(2.2 \times 10^{-3})[\text{C}_2\text{O}_4^{2-}] = 1.96 \times 10^{-8}$$

Equation:

$$[\text{C}_2\text{O}_4^{2-}] = \frac{1.96 \times 10^{-8}}{2.2 \times 10^{-3}} = 8.9 \times 10^{-6}$$

A concentration of $[\text{C}_2\text{O}_4^{2-}] = 8.9 \times 10^{-6} \text{ M}$ is necessary to initiate the precipitation of CaC_2O_4 under these conditions.

Check Your Learning

If a solution contains 0.0020 mol of CrO_4^{2-} per liter, what concentration of Ag^+ ion must be reached by adding solid AgNO_3 before Ag_2CrO_4 begins to precipitate? Neglect any increase in volume upon adding the solid silver nitrate.

Note:

Answer:

$$4.5 \times 10^{-9} \text{ M}$$

It is sometimes useful to know the concentration of an ion that remains in solution after precipitation. We can use the solubility product for this calculation too: If we know the value of K_{sp} and the concentration of one ion in solution, we can calculate the concentration of the second ion remaining in solution. The calculation is of the same type as that in [\[link\]](#)—calculation of the concentration of a species in an equilibrium mixture from the concentrations of the other species and the equilibrium constant. However, the concentrations are different; we are calculating concentrations after precipitation is complete, rather than at the start of precipitation.

Example:

Concentrations Following Precipitation

Clothing washed in water that has a manganese $[\text{Mn}^{2+}(\text{aq})]$ concentration exceeding 0.1 mg/L ($1.8 \times 10^{-6} \text{ M}$) may be stained by the manganese upon oxidation, but the amount of Mn^{2+} in the water can be reduced by adding a base. If a person doing laundry wishes to add a buffer to keep the pH high enough to precipitate the manganese as the hydroxide, $\text{Mn}(\text{OH})_2$, what pH is required to keep $[\text{Mn}^{2+}]$ equal to $1.8 \times 10^{-6} \text{ M}$?

Solution

The dissolution of $\text{Mn}(\text{OH})_2$ is described by the equation:

Equation:



We need to calculate the concentration of OH^{-} when the concentration of Mn^{2+} is $1.8 \times 10^{-6} \text{ M}$. From that, we calculate the pH. At equilibrium:

Equation:

$$K_{\text{sp}} = [\text{Mn}^{2+}][\text{OH}^{-}]^2$$

or

Equation:

$$(1.8 \times 10^{-6})[\text{OH}^-]^2 = 2 \times 10^{-13}$$

so

Equation:

$$[\text{OH}^-] = 3.3 \times 10^{-4} M$$

Now we calculate the pH from the pOH:

Equation:

$$\text{pOH} = -\log[\text{OH}^-] = -\log(3.3 \times 10^{-4}) = 3.48$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.48 = 10.52$$

If the person doing laundry adds a base, such as the sodium silicate (Na_4SiO_4) in some detergents, to the wash water until the pH is raised to 10.52, the manganese ion will be reduced to a concentration of $1.8 \times 10^{-6} M$; at that concentration or less, the ion will not stain clothing.

Check Your Learning

The first step in the preparation of magnesium metal is the precipitation of $\text{Mg}(\text{OH})_2$ from sea water by the addition of $\text{Ca}(\text{OH})_2$. The concentration of $\text{Mg}^{2+}(aq)$ in sea water is $5.37 \times 10^{-2} M$. Calculate the pH at which $[\text{Mg}^{2+}]$ is diminished to $1.0 \times 10^{-5} M$ by the addition of $\text{Ca}(\text{OH})_2$.

Note:

Answer:

10.97

Due to their light sensitivity, mixtures of silver halides are used in fiber optics for medical lasers, in photochromic eyeglass lenses (glass lenses that automatically darken when exposed to sunlight), and—before the advent of digital photography—in photographic film. Even though AgCl ($K_{\text{sp}} = 1.6 \times 10^{-10}$), AgBr ($K_{\text{sp}} = 5.0 \times 10^{-13}$), and AgI ($K_{\text{sp}} = 1.5 \times 10^{-16}$) are each quite insoluble, we cannot prepare a homogeneous solid mixture of them by adding Ag^+ to a solution of Cl^- , Br^- , and I^- ; essentially all of the AgI will precipitate before any of the other solid halides form because of its smaller value for K_{sp} . However, we can prepare a homogeneous mixture of the solids by slowly adding a solution of Cl^- , Br^- , and I^- to a solution of Ag^+ .

When two anions form slightly soluble compounds with the same cation, or when two cations form slightly soluble compounds with the same anion, the less soluble compound (usually, the compound with the smaller K_{sp}) generally precipitates first when we add a precipitating agent to a solution containing both anions (or both cations). When the K_{sp} values of the two compounds differ by two orders of magnitude or more (e.g., 10^{-2} vs. 10^{-4}), almost all of the less soluble compound precipitates before any of the more soluble one does. This is an example of **selective precipitation**, where a reagent is added to a solution of dissolved ions causing one of the ions to precipitate out before the rest.

Note:

The Role of Precipitation in Wastewater Treatment

Solubility equilibria are useful tools in the treatment of wastewater carried out in facilities that may treat the municipal water in your city or town ([link](#)). Specifically, selective precipitation is used to remove contaminants from wastewater before it is released back into natural bodies of water. For example, phosphate ions (PO_4^{3-}) are often present in the water discharged from manufacturing facilities. An abundance of phosphate causes excess

algae to grow, which impacts the amount of oxygen available for marine life as well as making water unsuitable for human consumption.



Wastewater treatment facilities, such as this one, remove contaminants from wastewater before the water is released back into the natural environment.
(credit: “eutrophication&hypoxia”/Wikimedia Commons)

One common way to remove phosphates from water is by the addition of calcium hydroxide, known as lime, $\text{Ca}(\text{OH})_2$. As the water is made more basic, the calcium ions react with phosphate ions to produce hydroxylapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, which then precipitates out of the solution:

Equation:



The precipitate is then removed by filtration and the water is brought back to a neutral pH by the addition of CO_2 in a recarbonation process. Other chemicals can also be used for the removal of phosphates by precipitation, including iron(III) chloride and aluminum sulfate.

View this [site](#) for more information on how phosphorus is removed from wastewater.

Selective precipitation can also be used in qualitative analysis. In this method, reagents are added to an unknown chemical mixture in order to induce precipitation. Certain reagents cause specific ions to precipitate out; therefore, the addition of the reagent can be used to determine whether the ion is present in the solution.

Note:



View this [simulation](#) to study the process of salts dissolving and forming saturated solutions and precipitates for specific compounds, or compounds for which you select the charges on the ions and the K_{sp}

Example:

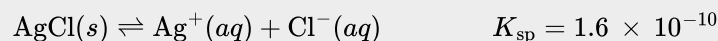
Precipitation of Silver Halides

A solution contains 0.0010 mol of KI and 0.10 mol of KCl per liter. AgNO_3 is gradually added to this solution. Which forms first, solid AgI or solid AgCl?

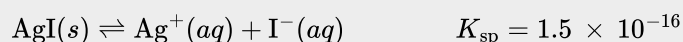
Solution

The two equilibria involved are:

Equation:



Equation:



If the solution contained about *equal* concentrations of Cl^- and I^- , then the silver salt with the smallest K_{sp} (AgI) would precipitate first. The concentrations are not equal, however, so we should find the $[\text{Ag}^+]$ at which AgCl begins to precipitate and the $[\text{Ag}^+]$ at which AgI begins to precipitate. The salt that forms at the lower $[\text{Ag}^+]$ precipitates first.

For AgI: AgI precipitates when Q equals K_{sp} for AgI (1.5×10^{-16}). When $[\text{I}^-] = 0.0010 \text{ M}$:

Equation:

$$Q = [\text{Ag}^+][\text{I}^-] = [\text{Ag}^+](0.0010) = 1.5 \times 10^{-16}$$

Equation:

$$[\text{Ag}^+] = \frac{1.5 \times 10^{-16}}{0.10} = 1.6 \times 10^{-9}$$

AgI begins to precipitate when $[\text{Ag}^+]$ is $1.6 \times 10^{-9} \text{ M}$.

For AgCl: AgCl precipitates when Q equals K_{sp} for AgCl (1.6×10^{-10}). When $[\text{Cl}^-] = 0.10 \text{ M}$:

Equation:

$$Q_{sp} = [\text{Ag}^+][\text{Cl}^-] = [\text{Ag}^+](0.10) = 1.6 \times 10^{-10}$$

Equation:

$$[\text{Ag}^+] = \frac{1.6 \times 10^{-10}}{0.10} = 1.6 \times 10^{-9} \text{ M}$$

AgCl begins to precipitate when $[\text{Ag}^+]$ is $1.6 \times 10^{-9} \text{ M}$.

AgI begins to precipitate at a lower $[\text{Ag}^+]$ than AgCl, so AgI begins to precipitate first.

Check Your Learning

If silver nitrate solution is added to a solution which is 0.050 M in both Cl^- and Br^- ions, at what $[\text{Ag}^+]$ would precipitation begin, and what would be the formula of the precipitate?

Note:

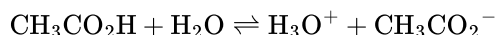
Answer:

$[\text{Ag}^+] = 1.0 \times 10^{-11} \text{ M}$; AgBr precipitates first

Common Ion Effect

As we saw when we discussed buffer solutions, the hydronium ion concentration of an aqueous solution of acetic acid decreases when the strong electrolyte sodium acetate, NaCH_3CO_2 , is added. We can explain this effect using Le Châtelier's principle. The addition of acetate ions causes the equilibrium to shift to the left, decreasing the concentration of H_3O^+ to compensate for the increased acetate ion concentration. This increases the concentration of $\text{CH}_3\text{CO}_2\text{H}$:

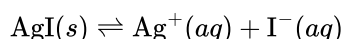
Equation:



Because sodium acetate and acetic acid have the acetate ion in common, the influence on the equilibrium is called the **common ion effect**.

The common ion effect can also have a direct effect on solubility equilibria. Suppose we are looking at the reaction where silver iodide is dissolved:

Equation:



If we were to add potassium iodide (KI) to this solution, we would be adding a substance that shares a common ion with silver iodide. Le Châtelier's principle tells us that when a change is made to a system at equilibrium, the reaction will shift to counteract that change. In this example, there would be an excess of iodide ions, so the reaction would shift toward the left, causing more silver iodide to precipitate out of solution.

Note:



View this [simulation](#) to see how the common ion effect works with different concentrations of salts.

Example:

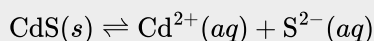
Common Ion Effect

Calculate the molar solubility of cadmium sulfide (CdS) in a $0.010\text{-}M$ solution of cadmium bromide (CdBr_2). The K_{sp} of CdS is 1.0×10^{-28} .

Solution

The first thing you should notice is that the cadmium sulfide is dissolved in a solution that contains cadmium ions. We need to use an ICE table to set up this problem and include the CdBr_2 concentration as a contributor of cadmium ions:

Equation:



	$\text{CdS (s)} \rightleftharpoons \text{Cd}^{2+} \text{ (aq)} + \text{S}^{2-} \text{ (aq)}$		
Initial concentration (M)		0.010	0
Change (M)		x	x
Equilibrium concentration (M)		$0.010 + x$	$0 + x = x$

Equation:

$$K_{\text{sp}} = [\text{Cd}^{2+}][\text{S}^{2-}] = 1.0 \times 10^{-28}$$

Equation:

$$(0.010 + x)(x) = 1.0 \times 10^{-28}$$

Equation:

$$x^2 + 0.010x - 1.0 \times 10^{-28} = 0$$

We can solve this equation using the quadratic formula, but we can also make an assumption to make this calculation much simpler. Since the K_{sp} value is so small compared with the cadmium concentration, we can assume that the change between the initial concentration and the equilibrium concentration is negligible, so that $0.010 + x \sim 0.010$. Going back to our K_{sp} expression, we would now get:

Equation:

$$K_{\text{sp}} = [\text{Cd}^{2+}][\text{S}^{2-}] = 1.0 \times 10^{-28}$$

Equation:

$$(0.010)(x) = 1.0 \times 10^{-28}$$

Equation:

$$x = 1.0 \times 10^{-26}$$

Therefore, the molar solubility of CdS in this solution is $1.0 \times 10^{-26} \text{ M}$.

Check Your Learning

Calculate the molar solubility of aluminum hydroxide, Al(OH)_3 , in a 0.015-M solution of aluminum nitrate, $\text{Al(NO}_3)_3$. The K_{sp} of Al(OH)_3 is 2×10^{-32} .

Note:

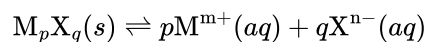
Answer:

$$4 \times 10^{-11} \text{ M}$$

Key Concepts and Summary

The equilibrium constant for an equilibrium involving the precipitation or dissolution of a slightly soluble ionic solid is called the solubility product, K_{sp} , of the solid. When we have a heterogeneous equilibrium involving the slightly soluble solid M_pX_q and its ions M^{m+} and X^{n-} :

Equation:



We write the solubility product expression as:

Equation:

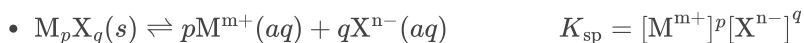
$$K_{sp} = [M^{m+}]^p [X^{n-}]^q$$

The solubility product of a slightly soluble electrolyte can be calculated from its solubility; conversely, its solubility can be calculated from its K_{sp} , provided the only significant reaction that occurs when the solid dissolves is the formation of its ions.

A slightly soluble electrolyte begins to precipitate when the magnitude of the reaction quotient for the dissolution reaction exceeds the magnitude of the solubility product. Precipitation continues until the reaction quotient equals the solubility product.

A reagent can be added to a solution of ions to allow one ion to selectively precipitate out of solution. The common ion effect can also play a role in precipitation reactions. In the presence of an ion in common with one of the ions in the solution, Le Châtelier's principle applies and more precipitate comes out of solution so that the molar solubility is reduced.

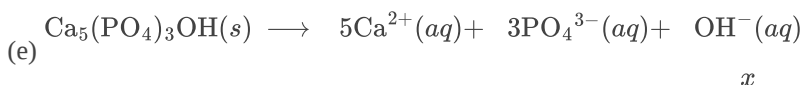
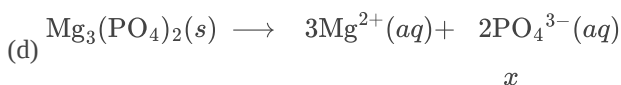
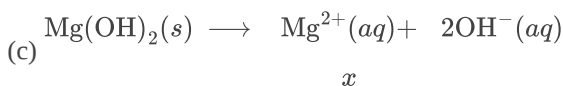
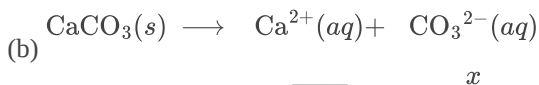
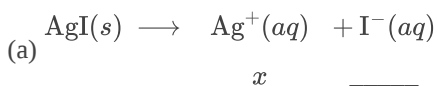
Key Equations

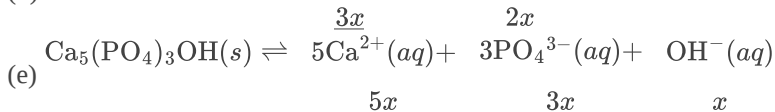
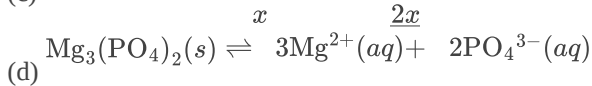
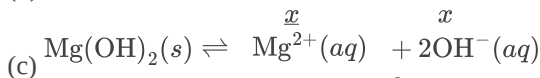
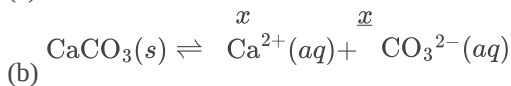
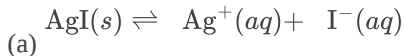


Chemistry End of Chapter Exercises

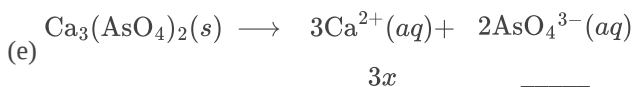
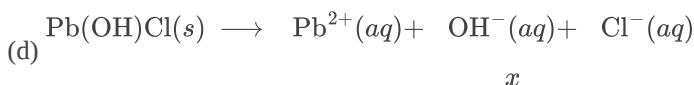
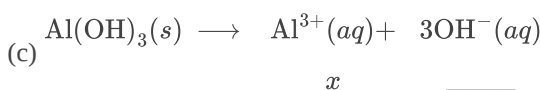
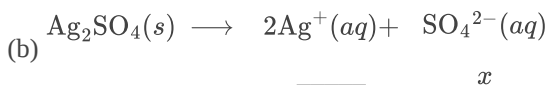
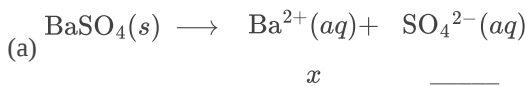
Exercise:

Problem: Complete the changes in concentrations for each of the following reactions:



Solution:**Exercise:**

Problem: Complete the changes in concentrations for each of the following reactions:

**Exercise:****Problem:**

How do the concentrations of Ag^+ and CrO_4^{2-} in a saturated solution above 1.0 g of solid Ag_2CrO_4 change when 100 g of solid Ag_2CrO_4 is added to the system? Explain.

Solution:

There is no change. A solid has an activity of 1 whether there is a little or a lot.

Exercise:**Problem:**

How do the concentrations of Pb^{2+} and S^{2-} change when K_2S is added to a saturated solution of PbS ?

Exercise:

Problem:

What additional information do we need to answer the following question: How is the equilibrium of solid silver bromide with a saturated solution of its ions affected when the temperature is raised?

Solution:

The solubility of silver bromide at the new temperature must be known. Normally the solubility increases and some of the solid silver bromide will dissolve.

Exercise:**Problem:**

Which of the following slightly soluble compounds has a solubility greater than that calculated from its solubility product because of hydrolysis of the anion present: CoSO_3 , CuI , PbCO_3 , PbCl_2 , Tl_2S , KClO_4 ?

Exercise:**Problem:**

Which of the following slightly soluble compounds has a solubility greater than that calculated from its solubility product because of hydrolysis of the anion present: AgCl , BaSO_4 , CaF_2 , Hg_2I_2 , MnCO_3 , ZnS , PbS ?

Solution:

CaF_2 , MnCO_3 , and ZnS

Exercise:**Problem:**

Write the ionic equation for dissolution and the solubility product (K_{sp}) expression for each of the following slightly soluble ionic compounds:

- (a) PbCl_2
- (b) Ag_2S
- (c) $\text{Sr}_3(\text{PO}_4)_2$
- (d) SrSO_4

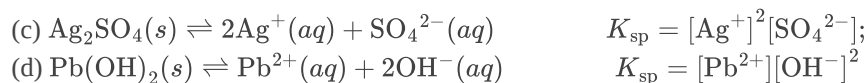
Exercise:**Problem:**

Write the ionic equation for the dissolution and the K_{sp} expression for each of the following slightly soluble ionic compounds:

- (a) LaF_3
 - (b) CaCO_3
 - (c) Ag_2SO_4
 - (d) $\text{Pb}(\text{OH})_2$
-

Solution:

- (a) $\text{LaF}_3(s) \rightleftharpoons \text{La}^{3+}(aq) + 3\text{F}^{-}(aq)$ $K_{\text{sp}} = [\text{La}^{3+}][\text{F}^{-}]^3$;
- (b) $\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq)$ $K_{\text{sp}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$;



Exercise:

Problem:

The [*Handbook of Chemistry and Physics*](#) gives solubilities of the following compounds in grams per 100 mL of water. Because these compounds are only slightly soluble, assume that the volume does not change on dissolution and calculate the solubility product for each.

- (a) BaSiF_6 , 0.026 g/100 mL (contains SiF_6^{2-} ions)
- (b) $\text{Ce}(\text{IO}_3)_4$, 1.5×10^{-2} g/100 mL
- (c) $\text{Gd}_2(\text{SO}_4)_3$, 3.98 g/100 mL
- (d) $(\text{NH}_4)_2\text{PtBr}_6$, 0.59 g/100 mL (contains PtBr_6^{2-} ions)

Exercise:

Problem:

The [*Handbook of Chemistry and Physics*](#) gives solubilities of the following compounds in grams per 100 mL of water. Because these compounds are only slightly soluble, assume that the volume does not change on dissolution and calculate the solubility product for each.

- (a) BaSeO_4 , 0.0118 g/100 mL
- (b) $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$, 0.30 g/100 mL
- (c) $\text{NH}_4\text{MgAsO}_4 \cdot 6\text{H}_2\text{O}$, 0.038 g/100 mL
- (d) $\text{La}_2(\text{MoO}_4)_3$, 0.00179 g/100 mL

Solution:

(a) 1.77×10^{-7} ; (b) 1.6×10^{-6} ; (c) 2.2×10^{-9} ; (d) 7.91×10^{-22}

Exercise:

Problem:

Use solubility products and predict which of the following salts is the most soluble, in terms of moles per liter, in pure water: CaF_2 , Hg_2Cl_2 , PbI_2 , or $\text{Sn}(\text{OH})_2$.

Exercise:

Problem:

Assuming that no equilibria other than dissolution are involved, calculate the molar solubility of each of the following from its solubility product:

- (a) $\text{KHC}_4\text{H}_4\text{O}_6$
- (b) PbI_2
- (c) $\text{Ag}_4[\text{Fe}(\text{CN})_6]$, a salt containing the $\text{Fe}(\text{CN})_4^-$ ion
- (d) Hg_2I_2

Solution:

- (a) $2 \times 10^{-2} M$; (b) $1.5 \times 10^{-3} M$; (c) $2.27 \times 10^{-9} M$; (d) $2.2 \times 10^{-10} M$

Exercise:

Problem:

Assuming that no equilibria other than dissolution are involved, calculate the molar solubility of each of the following from its solubility product:

- (a) Ag_2SO_4
 (b) PbBr_2
 (c) AgI
 (d) $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$

Exercise:

Problem:

Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that changes in the initial concentrations of the common ions can be neglected.

- (a) $\text{AgCl}(s)$ in $0.025 M \text{ NaCl}$
 (b) $\text{CaF}_2(s)$ in $0.00133 M \text{ KF}$
 (c) $\text{Ag}_2\text{SO}_4(s)$ in 0.500 L of a solution containing 19.50 g of K_2SO_4
 (d) $\text{Zn}(\text{OH})_2(s)$ in a solution buffered at a pH of 11.45

Solution:

- (a) $6.4 \times 10^{-9} M = [\text{Ag}^+]$, $[\text{Cl}^-] = 0.025 M$
 Check: $\frac{6.4 \times 10^{-9} M}{0.025 M} \times 100\% = 2.6 \times 10^{-5}\%$, an insignificant change;
 (b) $2.2 \times 10^{-5} M = [\text{Ca}^{2+}]$, $[\text{F}^-] = 0.0013 M$
 Check: $\frac{2.26 \times 10^{-5} M}{0.00133 M} \times 100\% = 1.70\%$. This value is less than 5% and can be ignored.
 (c) $0.2238 M = [\text{SO}_4^{2-}]$; $[\text{Ag}^+] = 7.4 \times 10^{-3} M$
 Check: $\frac{3.7 \times 10^{-3}}{0.2238} \times 100\% = 1.64 \times 10^{-2}\%$; the condition is satisfied.
 (d) $[\text{OH}^-] = 2.8 \times 10^{-3} M$; $5.7 \times 10^{-12} M = [\text{Zn}^{2+}]$
 Check: $\frac{5.7 \times 10^{-12}}{2.8 \times 10^{-3}} \times 100\% = 2.0 \times 10^{-7}\%$; x is less than 5% of $[\text{OH}^-]$ and is, therefore, negligible.

Exercise:

Problem:

Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that changes in the initial concentrations of the common ions can be neglected.

- (a) $\text{TlCl}(s)$ in $1.250 M \text{ HCl}$
 (b) $\text{PbI}_2(s)$ in $0.0355 M \text{ CaI}_2$
 (c) $\text{Ag}_2\text{CrO}_4(s)$ in 0.225 L of a solution containing 0.856 g of K_2CrO_4
 (d) $\text{Cd}(\text{OH})_2(s)$ in a solution buffered at a pH of 10.995

Exercise:**Problem:**

Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that it is not appropriate to neglect the changes in the initial concentrations of the common ions.

(a) $\text{TiCl}(s)$ in 0.025 M TiNO_3

(b) $\text{BaF}_2(s)$ in 0.0313 M KF

(c) MgC_2O_4 in 2.250 L of a solution containing 8.156 g of $\text{Mg}(\text{NO}_3)_2$

(d) $\text{Ca}(\text{OH})_2(s)$ in an unbuffered solution initially with a pH of 12.700

Solution:

(a) $[\text{Cl}^-] = 7.6 \times 10^{-3}\text{ M}$

Check: $\frac{7.6 \times 10^{-3}}{0.025} \times 100\% = 30\%$

This value is too large to drop x . Therefore solve by using the quadratic equation:

$[\text{Ti}^+] = 3.1 \times 10^{-2}\text{ M}$

$[\text{Cl}^-] = 6.1 \times 10^{-3}$

(b) $[\text{Ba}^{2+}] = 7.7 \times 10^{-4}\text{ M}$

Check: $\frac{7.7 \times 10^{-4}}{0.0313} \times 100\% = 2.4\%$

Therefore, the condition is satisfied.

$[\text{Ba}^{2+}] = 7.7 \times 10^{-4}\text{ M}$

$[\text{F}^-] = 0.0321\text{ M}$;

(c) $\text{Mg}(\text{NO}_3)_2 = 0.02444\text{ M}$

$[\text{C}_2\text{O}_4^{2-}] = 2.9 \times 10^{-5}$

Check: $\frac{2.9 \times 10^{-5}}{0.02444} \times 100\% = 0.12\%$

The condition is satisfied; the above value is less than 5%.

$[\text{C}_2\text{O}_4^{2-}] = 2.9 \times 10^{-5}\text{ M}$

$[\text{Mg}^{2+}] = 0.0244\text{ M}$

(d) $[\text{OH}^-] = 0.0501\text{ M}$

$[\text{Ca}^{2+}] = 3.15 \times 10^{-3}$

Check: $\frac{3.15 \times 10^{-3}}{0.050} \times 100\% = 6.28\%$

This value is greater than 5%, so a more exact method, such as successive approximations, must be used.

$[\text{Ca}^{2+}] = 2.8 \times 10^{-3}\text{ M}$

$[\text{OH}^-] = 0.053 \times 10^{-2}\text{ M}$

Exercise:

Problem: Explain why the changes in concentrations of the common ions in [\[link\]](#) can be neglected.

Exercise:

Problem: Explain why the changes in concentrations of the common ions in [\[link\]](#) cannot be neglected.

Solution:

The changes in concentration are greater than 5% and thus exceed the maximum value for disregarding the change.

Exercise:

Problem: Calculate the solubility of aluminum hydroxide, $\text{Al}(\text{OH})_3$, in a solution buffered at pH 11.00 .

Exercise:**Problem:**

Refer to [Appendix J](#) for solubility products for calcium salts. Determine which of the calcium salts listed is most soluble in moles per liter and which is most soluble in grams per liter.

Solution:

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is the most soluble Ca salt in mol/L, and it is also the most soluble Ca salt in g/L.

Exercise:**Problem:**

Most barium compounds are very poisonous; however, barium sulfate is often administered internally as an aid in the X-ray examination of the lower intestinal tract ([link](#)). This use of BaSO_4 is possible because of its low solubility. Calculate the molar solubility of BaSO_4 and the mass of barium present in 1.00 L of water saturated with BaSO_4 .

Exercise:**Problem:**

Public Health Service standards for drinking water set a maximum of 250 mg/L ($2.60 \times 10^{-3} \text{ M}$) of SO_4^{2-} because of its cathartic action (it is a laxative). Does natural water that is saturated with CaSO_4 (“gyp” water) as a result of passing through soil containing gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, meet these standards? What is the concentration of SO_4^{2-} in such water?

Solution:

$4.8 \times 10^{-3} \text{ M} = [\text{SO}_4^{2-}] = [\text{Ca}^{2+}]$; Since this concentration is higher than $2.60 \times 10^{-3} \text{ M}$, “gyp” water does not meet the standards.

Exercise:

Problem: Perform the following calculations:

- (a) Calculate $[\text{Ag}^+]$ in a saturated aqueous solution of AgBr .
- (b) What will $[\text{Ag}^+]$ be when enough KBr has been added to make $[\text{Br}^-] = 0.050 \text{ M}$?
- (c) What will $[\text{Br}^-]$ be when enough AgNO_3 has been added to make $[\text{Ag}^+] = 0.020 \text{ M}$?

Exercise:**Problem:**

The solubility product of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is 2.4×10^{-5} . What mass of this salt will dissolve in 1.0 L of 0.010 M SO_4^{2-} ?

Solution:

Mass ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) = 0.72 g/L

Exercise:**Problem:**

Assuming that no equilibria other than dissolution are involved, calculate the concentrations of ions in a saturated solution of each of the following (see [Appendix J](#) for solubility products).

- (a) TiCl
- (b) BaF_2
- (c) Ag_2CrO_4
- (d) $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$
- (e) the mineral anglesite, PbSO_4

Exercise:

Problem:

Assuming that no equilibria other than dissolution are involved, calculate the concentrations of ions in a saturated solution of each of the following (see [Appendix J](#) for solubility products):

- (a) AgI
- (b) Ag_2SO_4
- (c) $\text{Mn}(\text{OH})_2$
- (d) $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$
- (e) the mineral brucite, $\text{Mg}(\text{OH})_2$

Solution:

(a) $[\text{Ag}^+] = [\text{I}^-] = 1.3 \times 10^{-5} \text{ M}$; (b) $[\text{Ag}^+] = 2.88 \times 10^{-2} \text{ M}$, $[\text{SO}_4^{2-}] = 1.44 \times 10^{-2} \text{ M}$; (c) $[\text{Mn}^{2+}] = 3.7 \times 10^{-5} \text{ M}$, $[\text{OH}^-] = 7.4 \times 10^{-5} \text{ M}$; (d) $[\text{Sr}^{2+}] = 4.3 \times 10^{-2} \text{ M}$, $[\text{OH}^-] = 8.6 \times 10^{-2} \text{ M}$; (e) $[\text{Mg}^{2+}] = 1.3 \times 10^{-4} \text{ M}$, $[\text{OH}^-] = 2.6 \times 10^{-4} \text{ M}$.

Exercise:

Problem:

The following concentrations are found in mixtures of ions in equilibrium with slightly soluble solids. From the concentrations given, calculate K_{sp} for each of the slightly soluble solids indicated:

- (a) AgBr : $[\text{Ag}^+] = 5.7 \times 10^{-7} \text{ M}$, $[\text{Br}^-] = 5.7 \times 10^{-7} \text{ M}$
- (b) CaCO_3 : $[\text{Ca}^{2+}] = 5.3 \times 10^{-3} \text{ M}$, $[\text{CO}_3^{2-}] = 9.0 \times 10^{-7} \text{ M}$
- (c) PbF_2 : $[\text{Pb}^{2+}] = 2.1 \times 10^{-3} \text{ M}$, $[\text{F}^-] = 4.2 \times 10^{-3} \text{ M}$
- (d) Ag_2CrO_4 : $[\text{Ag}^+] = 5.3 \times 10^{-5} \text{ M}$, $3.2 \times 10^{-3} \text{ M}$
- (e) InF_3 : $[\text{In}^{3+}] = 2.3 \times 10^{-3} \text{ M}$, $[\text{F}^-] = 7.0 \times 10^{-3} \text{ M}$

Exercise:

Problem:

The following concentrations are found in mixtures of ions in equilibrium with slightly soluble solids. From the concentrations given, calculate K_{sp} for each of the slightly soluble solids indicated:

- (a) TiCl : $[\text{Ti}^+] = 1.21 \times 10^{-2} \text{ M}$, $[\text{Cl}^-] = 1.2 \times 10^{-2} \text{ M}$
- (b) $\text{Ce}(\text{IO}_3)_4$: $[\text{Ce}^{4+}] = 1.8 \times 10^{-4} \text{ M}$, $[\text{IO}_3^-] = 2.6 \times 10^{-13} \text{ M}$
- (c) $\text{Gd}_2(\text{SO}_4)_3$: $[\text{Gd}^{3+}] = 0.132 \text{ M}$, $[\text{SO}_4^{2-}] = 0.198 \text{ M}$

(d) Ag_2SO_4 : $[\text{Ag}^+] = 2.40 \times 10^{-2} \text{ M}$, $[\text{SO}_4^{2-}] = 2.05 \times 10^{-2} \text{ M}$

(e) BaSO_4 : $[\text{Ba}^{2+}] = 0.500 \text{ M}$, $[\text{SO}_4^{2-}] = 2.16 \times 10^{-10} \text{ M}$

Solution:

(a) 1.7×10^{-4} ; (b) 8.2×10^{-55} ; (c) 1.35×10^{-4} ; (d) 1.18×10^{-5} ; (e) 1.08×10^{-10}

Exercise:

Problem:

Which of the following compounds precipitates from a solution that has the concentrations indicated? (See [Appendix J](#) for K_{sp} values.)

(a) KClO_4 : $[\text{K}^+] = 0.01 \text{ M}$, $[\text{ClO}_4^-] = 0.01 \text{ M}$

(b) K_2PtCl_6 : $[\text{K}^+] = 0.01 \text{ M}$, $[\text{PtCl}_6^{2-}] = 0.01 \text{ M}$

(c) PbI_2 : $[\text{Pb}^{2+}] = 0.003 \text{ M}$, $[\text{I}^-] = 1.3 \times 10^{-3} \text{ M}$

(d) Ag_2S : $[\text{Ag}^+] = 1 \times 10^{-10} \text{ M}$, $[\text{S}^{2-}] = 1 \times 10^{-13} \text{ M}$

Exercise:

Problem:

Which of the following compounds precipitates from a solution that has the concentrations indicated? (See [Appendix J](#) for K_{sp} values.)

(a) CaCO_3 : $[\text{Ca}^{2+}] = 0.003 \text{ M}$, $[\text{CO}_3^{2-}] = 0.003 \text{ M}$

(b) Co(OH)_2 : $[\text{Co}^{2+}] = 0.01 \text{ M}$, $[\text{OH}^-] = 1 \times 10^{-7} \text{ M}$

(c) CaHPO_4 : $[\text{Ca}^{2+}] = 0.01 \text{ M}$, $[\text{HPO}_4^{2-}] = 2 \times 10^{-6} \text{ M}$

(d) $\text{Pb}_3(\text{PO}_4)_2$: $[\text{Pb}^{2+}] = 0.01 \text{ M}$, $[\text{PO}_4^{3-}] = 1 \times 10^{-13} \text{ M}$

Solution:

- (a) CaCO_3 does precipitate.
- (b) The compound does not precipitate.
- (c) The compound does not precipitate.
- (d) The compound precipitates.

Exercise:

Problem:

Calculate the concentration of Tl^+ when TlCl just begins to precipitate from a solution that is 0.0250 M in Cl^- .

Exercise:

Problem:

Calculate the concentration of sulfate ion when BaSO_4 just begins to precipitate from a solution that is 0.0758 M in Ba^{2+} .

Solution:

$3.03 \times 10^{-7} \text{ M}$

Exercise:

Problem:

Calculate the concentration of Sr^{2+} when SrF_2 starts to precipitate from a solution that is 0.0025 M in F^- .

Exercise:**Problem:**

Calculate the concentration of PO_4^{3-} when Ag_3PO_4 starts to precipitate from a solution that is 0.0125 M in Ag^+ .

Solution:

$$9.2 \times 10^{-13}\text{ M}$$

Exercise:**Problem:**

Calculate the concentration of F^- required to begin precipitation of CaF_2 in a solution that is 0.010 M in Ca^{2+} .

Exercise:**Problem:**

Calculate the concentration of Ag^+ required to begin precipitation of Ag_2CO_3 in a solution that is $2.50 \times 10^{-6}\text{ M}$ in CO_3^{2-} .

Solution:

$$[\text{Ag}^+] = 1.8 \times 10^{-3}\text{ M}$$

Exercise:

Problem: What $[\text{Ag}^+]$ is required to reduce $[\text{CO}_3^{2-}]$ to $8.2 \times 10^{-4}\text{ M}$ by precipitation of Ag_2CO_3 ?

Exercise:

Problem: What $[\text{F}^-]$ is required to reduce $[\text{Ca}^{2+}]$ to $1.0 \times 10^{-4}\text{ M}$ by precipitation of CaF_2 ?

Solution:

$$6.3 \times 10^{-4}$$

Exercise:**Problem:**

A volume of 0.800 L of a $2 \times 10^{-4}\text{-M}$ $\text{Ba}(\text{NO}_3)_2$ solution is added to 0.200 L of $5 \times 10^{-4}\text{ M}$ Li_2SO_4 . Does BaSO_4 precipitate? Explain your answer.

Exercise:**Problem:**

Perform these calculations for nickel(II) carbonate. (a) With what volume of water must a precipitate containing NiCO_3 be washed to dissolve 0.100 g of this compound? Assume that the wash water becomes saturated with NiCO_3 ($K_{\text{sp}} = 1.36 \times 10^{-7}$).

(b) If the NiCO_3 were a contaminant in a sample of CoCO_3 ($K_{\text{sp}} = 1.0 \times 10^{-12}$), what mass of CoCO_3 would have been lost? Keep in mind that both NiCO_3 and CoCO_3 dissolve in the same solution.

Solution:

(a) 2.25 L; (b) 7.2×10^{-7} g

Exercise:

Problem:

Iron concentrations greater than 5.4×10^{-6} M in water used for laundry purposes can cause staining. What $[\text{OH}^-]$ is required to reduce $[\text{Fe}^{2+}]$ to this level by precipitation of $\text{Fe}(\text{OH})_2$?

Exercise:

Problem:

A solution is 0.010 M in both Cu^{2+} and Cd^{2+} . What percentage of Cd^{2+} remains in the solution when 99.9% of the Cu^{2+} has been precipitated as CuS by adding sulfide?

Solution:

100% of it is dissolved

Exercise:

Problem:

A solution is 0.15 M in both Pb^{2+} and Ag^+ . If Cl^- is added to this solution, what is $[\text{Ag}^+]$ when PbCl_2 begins to precipitate?

Exercise:

Problem:

What reagent might be used to separate the ions in each of the following mixtures, which are 0.1 M with respect to each ion? In some cases it may be necessary to control the pH. (Hint: Consider the K_{sp} values given in [Appendix J](#).)

(a) Hg_2^{2+} and Cu^{2+}

(b) SO_4^{2-} and Cl^-

(c) Hg^{2+} and Co^{2+}

(d) Zn^{2+} and Sr^{2+}

(e) Ba^{2+} and Mg^{2+}

(f) CO_3^{2-} and OH^-

Solution:

(a) Hg_2^{2+} and Cu^{2+} : Add SO_4^{2-} .

(b) SO_4^{2-} and Cl^- : Add Ba^{2+} .

(c) Hg^{2+} and Co^{2+} : Add S^{2-} .

(d) Zn^{2+} and Sr^{2+} : Add OH^- until $[\text{OH}^-] = 0.050$ M.

(e) Ba^{2+} and Mg^{2+} : Add SO_4^{2-} .

(f) CO_3^{2-} and OH^- : Add Ba^{2+} .

Exercise:

Problem:

A solution contains 1.0×10^{-5} mol of KBr and 0.10 mol of KCl per liter. AgNO_3 is gradually added to this solution. Which forms first, solid AgBr or solid AgCl?

Exercise:

Problem:

A solution contains 1.0×10^{-2} mol of KI and 0.10 mol of KCl per liter. AgNO_3 is gradually added to this solution. Which forms first, solid AgI or solid AgCl?

Solution:

AgI will precipitate first.

Exercise:**Problem:**

The calcium ions in human blood serum are necessary for coagulation ([link](#)). Potassium oxalate, $\text{K}_2\text{C}_2\text{O}_4$, is used as an anticoagulant when a blood sample is drawn for laboratory tests because it removes the calcium as a precipitate of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. It is necessary to remove all but 1.0% of the Ca^{2+} in serum in order to prevent coagulation. If normal blood serum with a buffered pH of 7.40 contains 9.5 mg of Ca^{2+} per 100 mL of serum, what mass of $\text{K}_2\text{C}_2\text{O}_4$ is required to prevent the coagulation of a 10 mL blood sample that is 55% serum by volume? (All volumes are accurate to two significant figures. Note that the volume of serum in a 10-mL blood sample is 5.5 mL. Assume that the K_{sp} value for CaC_2O_4 in serum is the same as in water.)

Exercise:**Problem:**

About 50% of urinary calculi (kidney stones) consist of calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$. The normal mid range calcium content excreted in the urine is 0.10 g of Ca^{2+} per day. The normal mid range amount of urine passed may be taken as 1.4 L per day. What is the maximum concentration of phosphate ion that urine can contain before a calculus begins to form?

Solution:

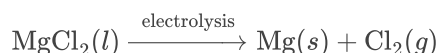
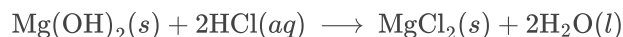
$$1.5 \times 10^{-12} \text{ M}$$

Exercise:**Problem:**

The pH of normal urine is 6.30, and the total phosphate concentration ($[\text{PO}_4^{3-}] + [\text{HPO}_4^{2-}] + [\text{H}_2\text{PO}_4^-] + [\text{H}_3\text{PO}_4]$) is 0.020 M. What is the minimum concentration of Ca^{2+} necessary to induce kidney stone formation? (See [link](#) for additional information.)

Exercise:**Problem:**

Magnesium metal (a component of alloys used in aircraft and a reducing agent used in the production of uranium, titanium, and other active metals) is isolated from sea water by the following sequence of reactions:



Sea water has a density of 1.026 g/cm^3 and contains 1272 parts per million of magnesium as $\text{Mg}^{2+}(\text{aq})$ by mass. What mass, in kilograms, of $\text{Ca}(\text{OH})_2$ is required to precipitate 99.9% of the magnesium in 1.00×10^3 L of sea water?

Solution:

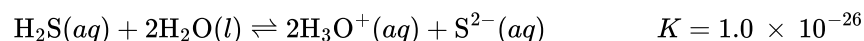
3.99 kg

Exercise:

Problem:

Hydrogen sulfide is bubbled into a solution that is 0.10 M in both Pb^{2+} and Fe^{2+} and 0.30 M in HCl. After the solution has come to equilibrium it is saturated with H_2S ($[\text{H}_2\text{S}] = 0.10 \text{ M}$). What concentrations of Pb^{2+} and Fe^{2+} remain in the solution? For a saturated solution of H_2S we can use the equilibrium:

Equation:



(Hint: The $[\text{H}_3\text{O}^+]$ changes as metal sulfides precipitate.)

Exercise:

Problem: Perform the following calculations involving concentrations of iodate ions:

(a) The iodate ion concentration of a saturated solution of $\text{La}(\text{IO}_3)_3$ was found to be $3.1 \times 10^{-3} \text{ mol/L}$. Find the K_{sp} .

(b) Find the concentration of iodate ions in a saturated solution of $\text{Cu}(\text{IO}_3)_2$ ($K_{\text{sp}} = 7.4 \times 10^{-8}$).

Solution:

(a) 3.1×10^{-11} ; (b) $[\text{Cu}^{2+}] = 2.6 \times 10^{-3}$; $[\text{IO}_3^-] = 5.3 \times 10^{-3}$

Exercise:

Problem: Calculate the molar solubility of AgBr in 0.035 M NaBr ($K_{\text{sp}} = 5 \times 10^{-13}$).

Exercise:

Problem:

How many grams of $\text{Pb}(\text{OH})_2$ will dissolve in 500 mL of a 0.050-M PbCl_2 solution ($K_{\text{sp}} = 1.2 \times 10^{-15}$)?

Solution:

$1.8 \times 10^{-5} \text{ g Pb}(\text{OH})_2$

Exercise:

Problem:

Use the [simulation](#) from the earlier Link to Learning to complete the following exercise:. Using 0.01 g CaF_2 , give the K_{sp} values found in a 0.2-M solution of each of the salts. Discuss why the values change as you change soluble salts.

Exercise:

Problem:

How many grams of Milk of Magnesia, $\text{Mg}(\text{OH})_2$ (s) (58.3 g/mol), would be soluble in 200 mL of water. $K_{\text{sp}} = 7.1 \times 10^{-12}$. Include the ionic reaction and the expression for K_{sp} in your answer. ($K_{\text{w}} = 1 \times 10^{-14} = [\text{H}_3\text{O}^+][\text{OH}^-]$)

Solution:



Exercise:

Problem:

Two hypothetical salts, LM₂ and LQ, have the same molar solubility in H₂O. If K_{sp} for LM₂ is 3.20×10^{-5} , what is the K_{sp} value for LQ?

Exercise:

Problem: Which of the following carbonates will form first? Which of the following will form last? Explain.

- (a) MgCO₃ $K_{\text{sp}} = 3.5 \times 10^{-8}$
- (b) CaCO₃ $K_{\text{sp}} = 4.2 \times 10^{-7}$
- (c) SrCO₃ $K_{\text{sp}} = 3.9 \times 10^{-9}$
- (d) BaCO₃ $K_{\text{sp}} = 4.4 \times 10^{-5}$
- (e) MnCO₃ $K_{\text{sp}} = 5.1 \times 10^{-9}$

Solution:

MnCO₃ will form first, since it has the smallest K_{sp} value it is the least soluble. MnCO₃ will be the last to precipitate, it has the largest K_{sp} value.

Exercise:

Problem:

How many grams of Zn(CN)₂(s) (117.44 g/mol) would be soluble in 100 mL of H₂O? Include the balanced reaction and the expression for K_{sp} in your answer. The K_{sp} value for Zn(CN)₂(s) is 3.0×10^{-16} .

Glossary

common ion effect

effect on equilibrium when a substance with an ion in common with the dissolved species is added to the solution; causes a decrease in the solubility of an ionic species, or a decrease in the ionization of a weak acid or base

molar solubility

solubility of a compound expressed in units of moles per liter (mol/L)

selective precipitation

process in which ions are separated using differences in their solubility with a given precipitating reagent

solubility product (K_{sp})

equilibrium constant for the dissolution of a slightly soluble electrolyte

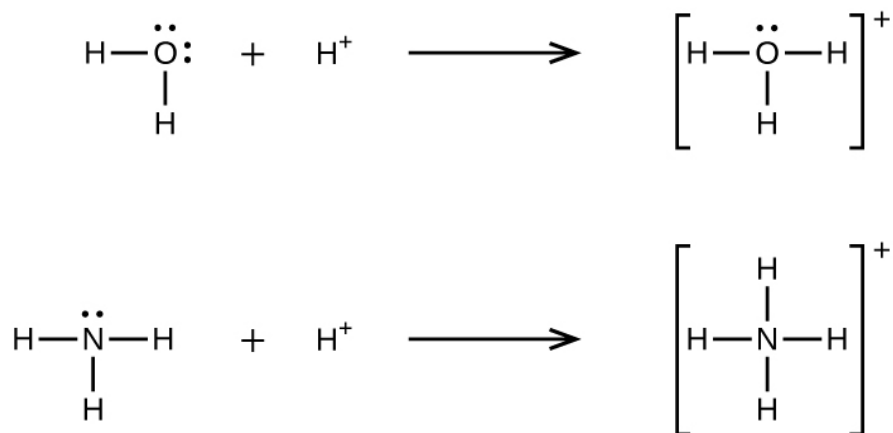
Lewis Acids and Bases

By the end of this section, you will be able to:

- Explain the Lewis model of acid-base chemistry
- Write equations for the formation of adducts and complex ions
- Perform equilibrium calculations involving formation constants

In 1923, G. N. Lewis proposed a generalized definition of acid-base behavior in which acids and bases are identified by their ability to accept or to donate a pair of electrons and form a coordinate covalent bond.

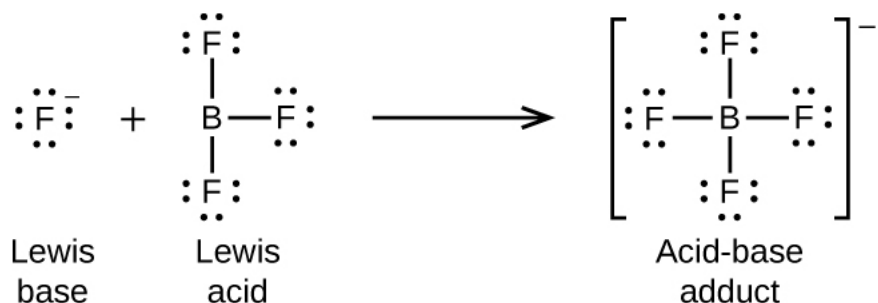
A **coordinate covalent bond** (or dative bond) occurs when one of the atoms in the bond provides both bonding electrons. For example, a coordinate covalent bond occurs when a water molecule combines with a hydrogen ion to form a hydronium ion. A coordinate covalent bond also results when an ammonia molecule combines with a hydrogen ion to form an ammonium ion. Both of these equations are shown here.



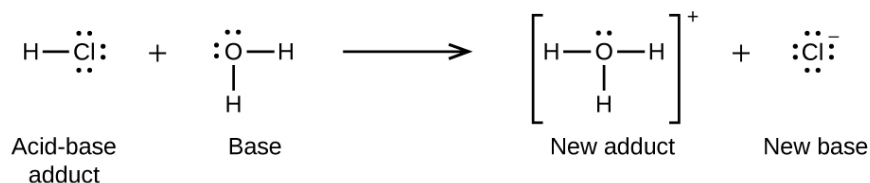
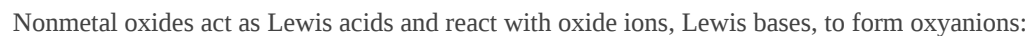
A **Lewis acid** is any species (molecule or ion) that can accept a pair of electrons, and a **Lewis base** is any species (molecule or ion) that can donate a pair of electrons.

A Lewis acid-base reaction occurs when a base donates a pair of electrons to an acid. A **Lewis acid-base adduct**, a compound that contains a coordinate covalent bond between the Lewis acid and the Lewis base, is formed. The following equations illustrate the general application of the Lewis concept.

The boron atom in boron trifluoride, BF_3 , has only six electrons in its valence shell. Being short of the preferred octet, BF_3 is a very good Lewis acid and reacts with many Lewis bases; a fluoride ion is the Lewis base in this reaction, donating one of its lone pairs:

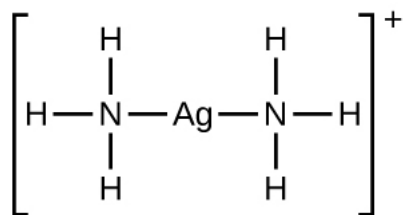


In the following reaction, each of two ammonia molecules, Lewis bases, donates a pair of electrons to a silver ion, the Lewis acid:



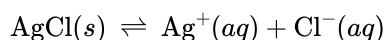
The last displacement reaction shows how the reaction of a Brønsted-Lowry acid with a base fits into the Lewis concept. A Brønsted-Lowry acid such as HCl is an acid-base adduct according to the Lewis concept, and proton transfer occurs because a more stable acid-base adduct is formed. Thus, although the definitions of acids and bases in the two theories are quite different, the theories overlap considerably.

Many slightly soluble ionic solids dissolve when the concentration of the metal ion in solution is decreased through the formation of complex (polyatomic) ions in a Lewis acid-base reaction. For example, silver chloride dissolves in a solution of ammonia because the silver ion reacts with ammonia to form the **complex ion** $\text{Ag}(\text{NH}_3)_2^+$. The Lewis structure of the $\text{Ag}(\text{NH}_3)_2^+$ ion is:

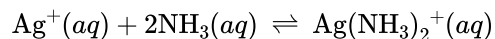


The equations for the dissolution of AgCl in a solution of NH_3 are:

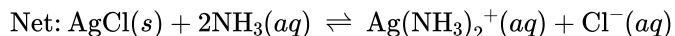
Equation:



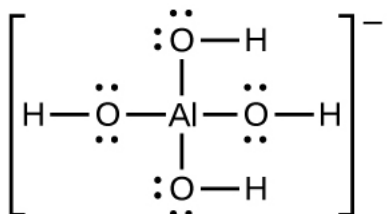
Equation:



Equation:

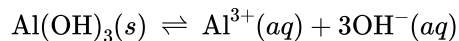


Aluminum hydroxide dissolves in a solution of sodium hydroxide or another strong base because of the formation of the complex ion $\text{Al}(\text{OH})_4^-$. The Lewis structure of the $\text{Al}(\text{OH})_4^-$ ion is:

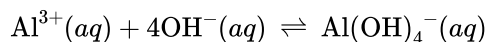


The equations for the dissolution are:

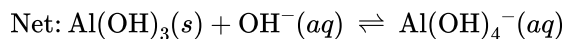
Equation:



Equation:

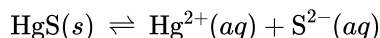


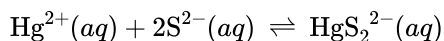
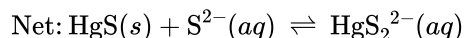
Equation:



Mercury(II) sulfide dissolves in a solution of sodium sulfide because HgS reacts with the S^{2-} ion:

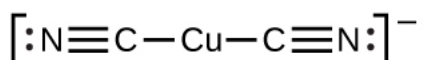
Equation:



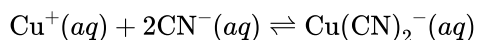
Equation:**Equation:**

A complex ion consists of a central atom, typically a transition metal cation, surrounded by ions, or molecules called **ligands**. These ligands can be neutral molecules like H_2O or NH_3 , or ions such as CN^- or OH^- . Often, the ligands act as Lewis bases, donating a pair of electrons to the central atom. The ligands form bonds with the central atom or ion, creating a new ion with a charge equal to the sum of the charges of the ligands and the central atom or ion. This more complex arrangement is why the resulting ion is called a *complex ion*. The complex ion formed in these reactions cannot be predicted; it must be determined experimentally. The types of bonds formed in complex ions are called coordinate covalent bonds, as electrons from the ligands are being shared with the central atom. Because of this, complex ions are sometimes referred to as coordination complexes. This will be studied further in upcoming chapters.

The equilibrium constant for the reaction of the components of a complex ion to form the complex ion in solution is called a **formation constant (K_f)** (sometimes called a stability constant). For example, the complex ion $\text{Cu}(\text{CN})_2^-$ is shown here:



It forms by the reaction:

Equation:

At equilibrium:

Equation:

$$K_f = Q = \frac{[\text{Cu}(\text{CN})_2^-]}{[\text{Cu}^+][\text{CN}^-]^2}$$

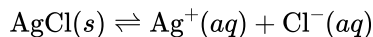
The inverse of the formation constant is the **dissociation constant (K_d)**, the equilibrium constant for the *decomposition* of a complex ion into its components in solution. We will work with dissociation constants further in the exercises for this section. [Appendix K](#) and [\[link\]](#) are tables of formation constants. In general, the larger the formation constant, the more stable the complex.

Common Complex Ions by Decreasing Formation Constants	
Substance	K_f at 25 °C
AlF_6^{3-}	7×10^{19}
$\text{Ag}(\text{NH}_3)_2^+$	1.7×10^7

Common Complex Ions by Decreasing Formation Constants	
Substance	K_f at 25 °C
$\text{Cd}(\text{CN})_4^{2-}$	3×10^{18}

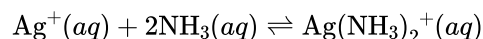
As an example of dissolution by complex ion formation, let us consider what happens when we add aqueous ammonia to a mixture of silver chloride and water. Silver chloride dissolves slightly in water, giving a small concentration of Ag^+ ($[\text{Ag}^+] = 1.3 \times 10^{-5} \text{ M}$):

Equation:



However, if NH_3 is present in the water, the complex ion, $\text{Ag}(\text{NH}_3)_2^+$, can form according to the equation:

Equation:



with

Equation:

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = 1.7 \times 10^7$$

The large size of this formation constant indicates that most of the free silver ions produced by the dissolution of AgCl combine with NH_3 to form $\text{Ag}(\text{NH}_3)_2^+$. As a consequence, the concentration of silver ions, $[\text{Ag}^+]$, is reduced, and the reaction quotient for the dissolution of silver chloride, $[\text{Ag}^+][\text{Cl}^-]$, falls below the solubility product of AgCl :

Equation:

$$Q = [\text{Ag}^+][\text{Cl}^-] < K_{\text{sp}}$$

More silver chloride then dissolves. If the concentration of ammonia is great enough, all of the silver chloride dissolves.

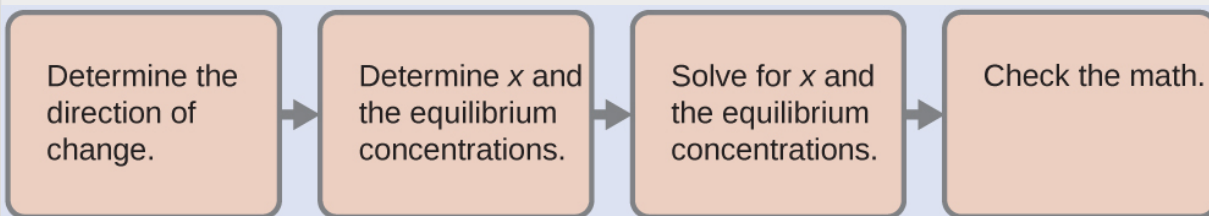
Example:

Dissociation of a Complex Ion

Calculate the concentration of the silver ion in a solution that initially is 0.10 M with respect to $\text{Ag}(\text{NH}_3)_2^+$.

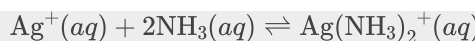
Solution

We use the familiar path to solve this problem:



Equation:

Determine the direction of change. The complex ion $\text{Ag}(\text{NH}_3)_2^+$ is in equilibrium with its components, as represented by the equation:



We write the equilibrium as a formation reaction because [Appendix K](#) lists formation constants for complex ions. Before equilibrium, the reaction quotient is larger than the equilibrium constant [$K_f = 1.7 \times 10^7$, and $Q = \frac{0.10}{0 \times 0}$, it is infinitely large], so the reaction shifts to the left to reach equilibrium.

Determine x and equilibrium concentrations. We let the change in concentration of Ag^+ be x . Dissociation of 1 mol of $\text{Ag}(\text{NH}_3)_2^+$ gives 1 mol of Ag^+ and 2 mol of NH_3 , so the change in $[\text{NH}_3]$ is $2x$ and that of $\text{Ag}(\text{NH}_3)_2^+$ is $-x$. In summary:

	Ag^+	+	2NH_3	\rightleftharpoons	$\text{Ag}(\text{NH}_3)_2^+$
Initial concentration (M)	0		0		0.10
Change (M)	x		$2x$		$-x$
Equilibrium concentration (M)	$0 + x$		$0 + 2x$		$0.10 - x$

Equation:

Equation:

Equation:

Equation:

Solve for x and the equilibrium concentrations. At equilibrium:

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2}$$

$$1.7 \times 10^7 = \frac{0.10 - x}{(x)(2x)^2}$$

Both Q and K_f are much larger than 1, so let us assume that the changes in concentrations needed to reach equilibrium are small. Thus $0.10 - x$ is approximated as 0.10:

$$1.7 \times 10^7 = \frac{0.10}{(x)(2x)^2} x^3 = \frac{0.1}{4(1.7 \times 10^7)}$$

Check the work. The value of Q calculated using the equilibrium concentrations is equal to K_f within the error associated with the significant figures in the calculation.

Check Your Learning

Calculate the silver ion concentration, $[\text{Ag}^+]$, of a solution prepared by dissolving 1.00 g of AgNO_3 and 10.0 g of KCN in sufficient water to make 1.00 L of solution. (Hint: Because $Q < K_f$, assume the reaction goes to completion then calculate the $[\text{Ag}^+]$ produced by dissociation of the complex.)

Note:

Answer:

$$2.5 \times 10^{-22} \text{ M}$$

Key Concepts and Summary

G.N. Lewis proposed a definition for acids and bases that relies on an atom's or molecule's ability to accept or donate electron pairs. A Lewis acid is a species that can accept an electron pair, whereas a Lewis base has an electron pair available for donation to a Lewis acid. Complex ions are examples of Lewis acid-base adducts. In a complex ion, we have a central atom, often consisting of a transition metal cation, which acts as a Lewis acid, and several neutral molecules or ions surrounding them called ligands that act as Lewis bases. Complex ions form by sharing electron pairs to form coordinate covalent bonds. The equilibrium reaction that occurs when forming a

complex ion has an equilibrium constant associated with it called a formation constant, K_f . This is often referred to as a stability constant, as it represents the stability of the complex ion. Formation of complex ions in solution can have a profound effect on the solubility of a transition metal compound.

Chemistry End of Chapter Exercises

Exercise:

Problem: Under what circumstances, if any, does a sample of solid AgCl completely dissolve in pure water?

Solution:

when the amount of solid is so small that a saturated solution is not produced

Exercise:

Problem:

Explain why the addition of NH_3 or HNO_3 to a saturated solution of Ag_2CO_3 in contact with solid Ag_2CO_3 increases the solubility of the solid.

Exercise:

Problem:

Calculate the cadmium ion concentration, $[\text{Cd}^{2+}]$, in a solution prepared by mixing 0.100 L of 0.0100 M $\text{Cd}(\text{NO}_3)_2$ with 1.150 L of 0.100 M $\text{NH}_3(aq)$.

Solution:

$$8 \times 10^{-5} \text{ M}$$

Exercise:

Problem:

Explain why addition of NH_3 or HNO_3 to a saturated solution of $\text{Cu}(\text{OH})_2$ in contact with solid $\text{Cu}(\text{OH})_2$ increases the solubility of the solid.

Exercise:

Problem:

Sometimes equilibria for complex ions are described in terms of dissociation constants, K_d . For the complex ion AlF_6^{3-} the dissociation reaction is:



Calculate the value of the formation constant, K_f , for AlF_6^{3-} .

Solution:

$$5 \times 10^{23}$$

Exercise:

Problem:

Using the value of the formation constant for the complex ion $\text{Co}(\text{NH}_3)_6^{2+}$, calculate the dissociation constant.

Exercise:

Problem:

Using the dissociation constant, $K_d = 7.8 \times 10^{-18}$, calculate the equilibrium concentrations of Cd^{2+} and CN^- in a 0.250-M solution of $\text{Cd}(\text{CN})_4^{2-}$.

Solution:

	$[\text{Cd}(\text{CN})_4^{2-}]$	$[\text{CN}^-]$	$[\text{Cd}^{2+}]$
Initial concentration (M)	0.250	0	0
Equilibrium (M)	$0.250 - x$	$4x$	x

$$[\text{Cd}^{2+}] = 9.5 \times 10^{-5} \text{ M}; [\text{CN}^-] = 3.8 \times 10^{-4} \text{ M}$$

Exercise:**Problem:**

Using the dissociation constant, $K_d = 3.4 \times 10^{-15}$, calculate the equilibrium concentrations of Zn^{2+} and OH^- in a 0.0465-M solution of $\text{Zn}(\text{OH})_4^{2-}$.

Exercise:**Problem:**

Using the dissociation constant, $K_d = 2.2 \times 10^{-34}$, calculate the equilibrium concentrations of Co^{3+} and NH_3 in a 0.500-M solution of $\text{Co}(\text{NH}_3)_6^{3+}$.

Solution:

$$[\text{Co}^{3+}] = 3.0 \times 10^{-6} \text{ M}; [\text{NH}_3] = 1.8 \times 10^{-5} \text{ M}$$

Exercise:**Problem:**

Using the dissociation constant, $K_d = 1 \times 10^{-44}$, calculate the equilibrium concentrations of Fe^{3+} and CN^- in a 0.333 M solution of $\text{Fe}(\text{CN})_6^{3-}$.

Exercise:**Problem:**

Calculate the mass of potassium cyanide ion that must be added to 100 mL of solution to dissolve 2.0×10^{-2} mol of silver cyanide, AgCN .

Solution:

$$1.3 \text{ g}$$

Exercise:

Problem:

Calculate the minimum concentration of ammonia needed in 1.0 L of solution to dissolve 3.0×10^{-3} mol of silver bromide.

Exercise:**Problem:**

A roll of 35-mm black and white photographic film contains about 0.27 g of unexposed AgBr before developing. What mass of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (sodium thiosulfate pentahydrate or hypo) in 1.0 L of developer is required to dissolve the AgBr as $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ ($K_f = 4.7 \times 10^{13}$)?

Solution:

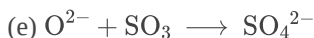
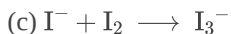
0.79 g

Exercise:**Problem:**

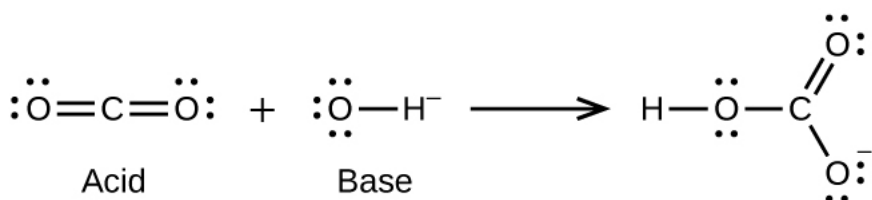
We have seen an introductory definition of an acid: An acid is a compound that reacts with water and increases the amount of hydronium ion present. In the chapter on acids and bases, we saw two more definitions of acids: a compound that donates a proton (a hydrogen ion, H^+) to another compound is called a Brønsted-Lowry acid, and a Lewis acid is any species that can accept a pair of electrons. Explain why the introductory definition is a macroscopic definition, while the Brønsted-Lowry definition and the Lewis definition are microscopic definitions.

Exercise:**Problem:**

Write the Lewis structures of the reactants and product of each of the following equations, and identify the Lewis acid and the Lewis base in each:

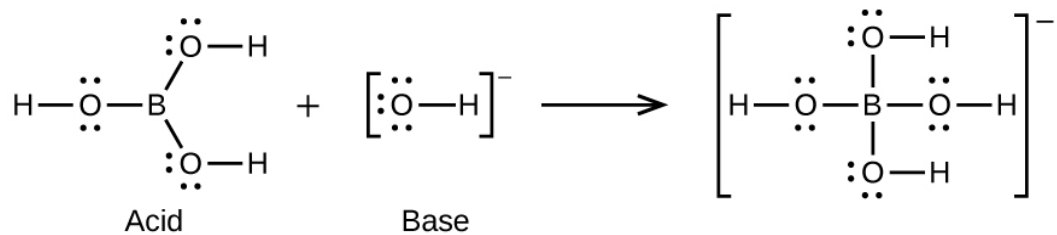
**Solution:**

(a)

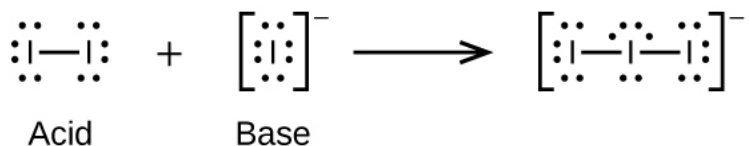


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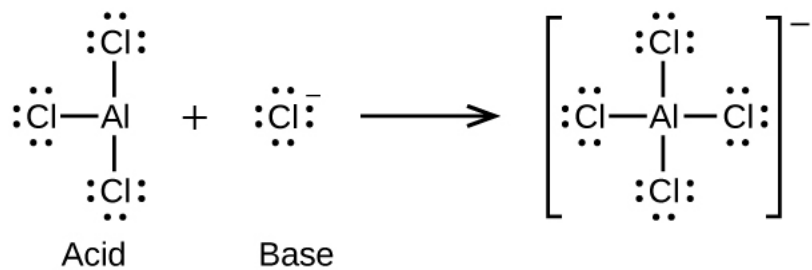
(b)



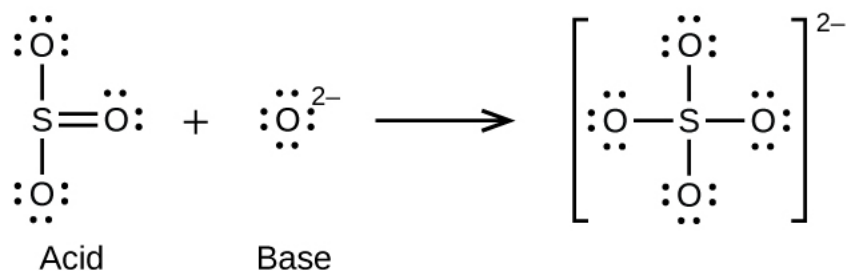
;
(c)



;
(d)



;
(e)

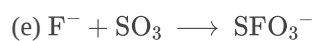


Exercise:

Problem:

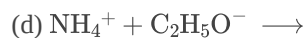
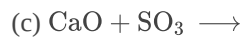
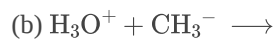
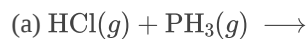
Write the Lewis structures of the reactants and product of each of the following equations, and identify the Lewis acid and the Lewis base in each:





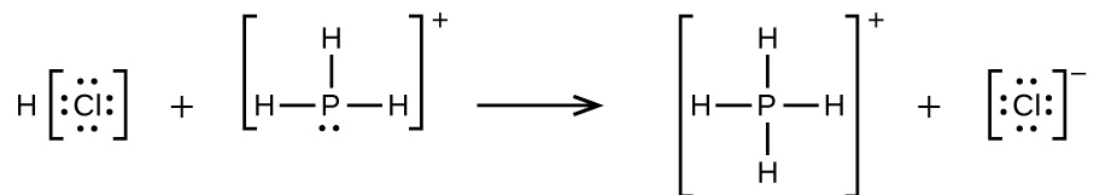
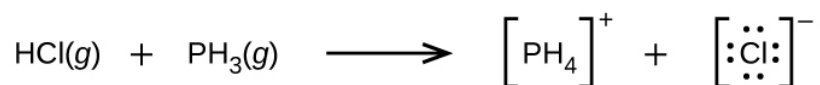
Exercise:

Problem: Using Lewis structures, write balanced equations for the following reactions:

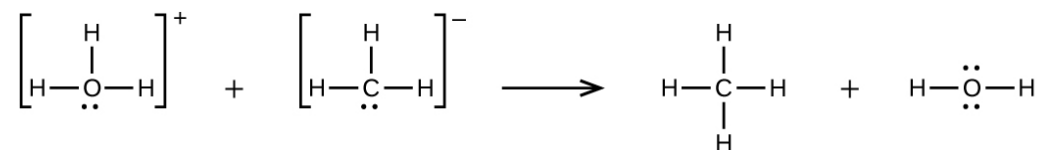
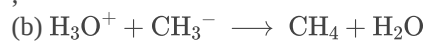


Solution:

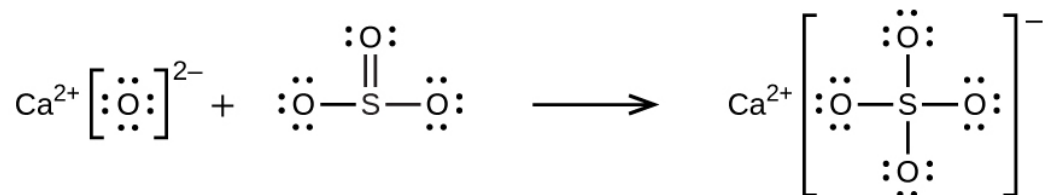
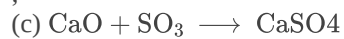
(a)



;

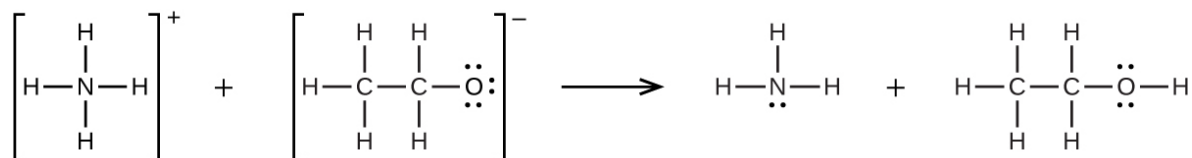


;



;





Exercise:

Problem:

Calculate $[\text{HgCl}_4^{2-}]$ in a solution prepared by adding 0.0200 mol of NaCl to 0.250 L of a 0.100-M HgCl_2 solution.

Exercise:

Problem:

In a titration of cyanide ion, 28.72 mL of 0.0100 M AgNO_3 is added before precipitation begins. [The reaction of Ag^+ with CN^- goes to completion, producing the $\text{Ag}(\text{CN})_2^-$ complex.] Precipitation of solid AgCN takes place when excess Ag^+ is added to the solution, above the amount needed to complete the formation of $\text{Ag}(\text{CN})_2^-$. How many grams of NaCN were in the original sample?

Solution:

0.0281 g

Exercise:

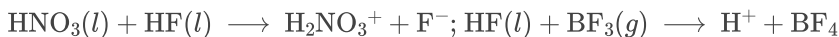
Problem: What are the concentrations of Ag^+ , CN^- , and $\text{Ag}(\text{CN})_2^-$ in a saturated solution of AgCN ?

Exercise:

Problem:

In dilute aqueous solution HF acts as a weak acid. However, pure liquid HF (boiling point = 19.5 °C) is a strong acid. In liquid HF, HNO_3 acts like a base and accepts protons. The acidity of liquid HF can be increased by adding one of several inorganic fluorides that are Lewis acids and accept F^- ion (for example, BF_3 or SbF_5). Write balanced chemical equations for the reaction of pure HNO_3 with pure HF and of pure HF with BF_3 .

Solution:



Exercise:

Problem:

The simplest amino acid is glycine, $\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$. The common feature of amino acids is that they contain the functional groups: an amine group, $-\text{NH}_2$, and a carboxylic acid group, $-\text{CO}_2\text{H}$. An amino acid can function as either an acid or a base. For glycine, the acid strength of the carboxyl group is about the same as that of acetic acid, $\text{CH}_3\text{CO}_2\text{H}$, and the base strength of the amino group is slightly greater than that of ammonia, NH_3 .

(a) Write the Lewis structures of the ions that form when glycine is dissolved in 1 M HCl and in 1 M KOH.

(b) Write the Lewis structure of glycine when this amino acid is dissolved in water. (Hint: Consider the relative base strengths of the $-\text{NH}_2$ and $-\text{CO}_2^-$ groups.)

Exercise:

Problem: Boric acid, H_3BO_3 , is not a Brønsted-Lowry acid but a Lewis acid.

(a) Write an equation for its reaction with water.

(b) Predict the shape of the anion thus formed.

(c) What is the hybridization on the boron consistent with the shape you have predicted?

Solution:

(a) $\text{H}_3\text{BO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_4\text{BO}_4^- + \text{H}^+$; (b) The electronic and molecular shapes are the same—both tetrahedral. (c) The tetrahedral structure is consistent with sp^3 hybridization.

Glossary

complex ion

ion consisting of a transition metal central atom and surrounding molecules or ions called ligands

coordinate covalent bond

(also, dative bond) bond formed when one atom provides both electrons in a shared pair

dissociation constant

(K_d) equilibrium constant for the decomposition of a complex ion into its components in solution

formation constant

(K_f) (also, stability constant) equilibrium constant for the formation of a complex ion from its components in solution

Lewis acid

any species that can accept a pair of electrons and form a coordinate covalent bond

Lewis acid-base adduct

compound or ion that contains a coordinate covalent bond between a Lewis acid and a Lewis base

Lewis base

any species that can donate a pair of electrons and form a coordinate covalent bond

ligand

molecule or ion that surrounds a transition metal and forms a complex ion; ligands act as Lewis bases

Multiple Equilibria

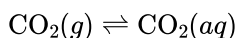
By the end of this section, you will be able to:

- Describe examples of systems involving two (or more) simultaneous chemical equilibria
- Calculate reactant and product concentrations for multiple equilibrium systems
- Compare dissolution and weak electrolyte formation

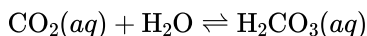
There are times when one equilibrium reaction does not adequately describe the system being studied. Sometimes we have more than one type of equilibrium occurring at once (for example, an acid-base reaction and a precipitation reaction).

The ocean is a unique example of a system with **multiple equilibria**, or multiple states of solubility equilibria working simultaneously. Carbon dioxide in the air dissolves in sea water, forming carbonic acid (H_2CO_3). The carbonic acid then ionizes to form hydrogen ions and bicarbonate ions (HCO_3^-), which can further ionize into more hydrogen ions and carbonate ions (CO_3^{2-}):

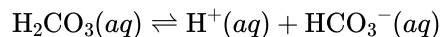
Equation:



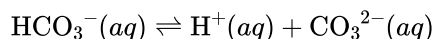
Equation:



Equation:



Equation:



The excess H^+ ions make seawater more acidic. Increased ocean acidification can then have negative impacts on reef-building coral, as they cannot absorb the calcium carbonate they need to grow and maintain their skeletons ([link](#)). This in turn disrupts the local biosystem that depends upon the health of the reefs for its survival. If enough local reefs are similarly affected, the disruptions to sea life can be felt globally. The world's oceans are presently in the midst of a period of intense acidification, believed to have begun in the mid-nineteenth century, and which is now accelerating at a rate faster than any change to oceanic pH in the last 20 million years.



(a)



(b)

Healthy coral reefs (a) support a dense and diverse array of sea life across the ocean food chain. But when coral are unable to adequately build and maintain their calcium carbonate skeletons because of excess ocean

acidification, the unhealthy reef (b) is only capable of hosting a small fraction of the species as before, and the local food chain starts to collapse. (credit a: modification of work by NOAA Photo Library; credit b: modification of work by “prilfish”/Flickr)

Note:

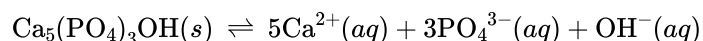


Learn more about ocean [acidification](#) and how it affects other marine creatures. This [site](#) has detailed information about how ocean acidification specifically affects coral reefs.

Slightly soluble solids derived from weak acids generally dissolve in strong acids, unless their solubility products are extremely small. For example, we can dissolve CuCO_3 , FeS , and $\text{Ca}_3(\text{PO}_4)_2$ in HCl because their basic anions react to form weak acids (H_2CO_3 , H_2S , and H_2PO_4^-). The resulting decrease in the concentration of the anion results in a shift of the equilibrium concentrations to the right in accordance with Le Châtelier's principle.

Of particular relevance to us is the dissolution of hydroxylapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, in acid. Apatites are a class of calcium phosphate minerals ([link](#)); a biological form of hydroxylapatite is found as the principal mineral in the enamel of our teeth. A mixture of hydroxylapatite and water (or saliva) contains an equilibrium mixture of solid $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ and dissolved Ca^{2+} , PO_4^{3-} , and OH^- ions:

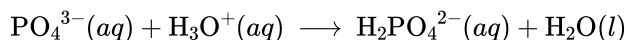
Equation:



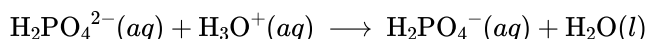
Crystal of the mineral hydroxylapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, is shown here. Pure apatite is white, but like many other minerals, this sample is colored because of the presence of impurities.

When exposed to acid, phosphate ions react with hydronium ions to form hydrogen phosphate ions and ultimately, phosphoric acid:

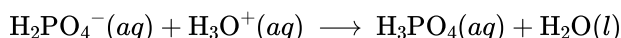
Equation:



Equation:

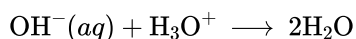


Equation:



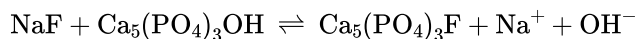
Hydroxide ion reacts to form water:

Equation:



These reactions decrease the phosphate and hydroxide ion concentrations, and additional hydroxylapatite dissolves in an acidic solution in accord with Le Châtelier's principle. Our teeth develop cavities when acid waste produced by bacteria growing on them causes the hydroxylapatite of the enamel to dissolve. Fluoride toothpastes contain sodium fluoride, NaF, or stannous fluoride [more properly named tin(II) fluoride], SnF_2 . They function by replacing the OH^- ion in hydroxylapatite with F^- ion, producing fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$:

Equation:



The resulting $\text{Ca}_5(\text{PO}_4)_3\text{F}$ is slightly less soluble than $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, and F^- is a weaker base than OH^- . Both of these factors make the fluorapatite more resistant to attack by acids than hydroxylapatite. See the Chemistry in Everyday Life feature on the role of fluoride in preventing tooth decay for more information.

Note:

Role of Fluoride in Preventing Tooth Decay

As we saw previously, fluoride ions help protect our teeth by reacting with hydroxylapatite to form fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$. Since it lacks a hydroxide ion, fluorapatite is more resistant to attacks by acids in our mouths and is thus less soluble, protecting our teeth. Scientists discovered that naturally fluorinated water could be beneficial to your teeth, and so it became common practice to add fluoride to drinking water. Toothpastes and mouthwashes also contain amounts of fluoride ([link](#)).

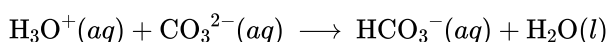


Fluoride, found in many toothpastes, helps prevent tooth decay (credit: Kerry Ceszyk).

Unfortunately, excess fluoride can negate its advantages. Natural sources of drinking water in various parts of the world have varying concentrations of fluoride, and places where that concentration is high are prone to certain health risks when there is no other source of drinking water. The most serious side effect of excess fluoride is the bone disease, skeletal fluorosis. When excess fluoride is in the body, it can cause the joints to stiffen and the bones to thicken. It can severely impact mobility and can negatively affect the thyroid gland. Skeletal fluorosis is a condition that over 2.7 million people suffer from across the world. So while fluoride can protect our teeth from decay, the US Environmental Protection Agency sets a maximum level of 4 ppm (4 mg/L) of fluoride in drinking water in the US. Fluoride levels in water are not regulated in all countries, so fluorosis is a problem in areas with high levels of fluoride in the groundwater.

When acid rain attacks limestone or marble, which are calcium carbonates, a reaction occurs that is similar to the acid attack on hydroxylapatite. The hydronium ion from the acid rain combines with the carbonate ion from calcium carbonates and forms the hydrogen carbonate ion, a weak acid:

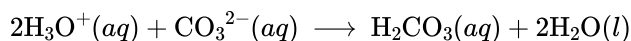
Equation:



Calcium hydrogen carbonate, $\text{Ca}(\text{HCO}_3)_2$, is soluble, so limestone and marble objects slowly dissolve in acid rain.

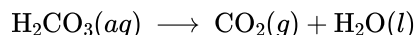
If we add calcium carbonate to a concentrated acid, hydronium ion reacts with the carbonate ion according to the equation:

Equation:



(Acid rain is usually not sufficiently acidic to cause this reaction; however, laboratory acids are.) The solution may become saturated with the weak electrolyte carbonic acid, which is unstable, and carbon dioxide gas can be evolved:

Equation:



These reactions decrease the carbonate ion concentration, and additional calcium carbonate dissolves. If enough acid is present, the concentration of carbonate ion is reduced to such a low level that the reaction quotient for the dissolution of calcium carbonate remains less than the solubility product of calcium carbonate, even after all of the calcium carbonate has dissolved.

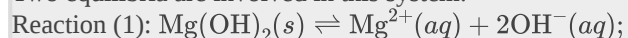
Example:

Prevention of Precipitation of $\text{Mg}(\text{OH})_2$

Calculate the concentration of ammonium ion that is required to prevent the precipitation of $\text{Mg}(\text{OH})_2$ in a solution with $[\text{Mg}^{2+}] = 0.10\text{ M}$ and $[\text{NH}_3] = 0.10\text{ M}$.

Solution

Two equilibria are involved in this system:



$$K_{\text{sp}} = 8.9 \times 10^{-12}$$



$$K_{\text{b}} = 1.8 \times 10^{-5}$$

To prevent the formation of solid $\text{Mg}(\text{OH})_2$, we must adjust the concentration of OH^- so that the reaction quotient for Equation (1), $Q = [\text{Mg}^{2+}][\text{OH}^-]^2$, is less than K_{sp} for $\text{Mg}(\text{OH})_2$. (To simplify the calculation, we determine the concentration of OH^- when $Q = K_{\text{sp}}$.) $[\text{OH}^-]$ can be reduced by the addition of NH_4^+ , which shifts Reaction (2) to the left and reduces $[\text{OH}^-]$.

Equation:

We determine

the $[\text{OH}^-]$ at $Q = [\text{Mg}^{2+}][\text{OH}^-]^2 = (0.10)[\text{OH}^-]^2 = 8.9 \times 10^{-12}$

which $Q =$

K_{sp} when

$[\text{Mg}^{2+}] =$

0.10 M:

Equation:

Solid $\text{Mg}(\text{OH})_2$

will not form in this solution

when $[\text{OH}^-]$ is

less than $9.4 \times$

10^{-6} M.

Equation:

We calculate the

$[\text{NH}_4^+]$ needed to

decrease $[\text{OH}^-]$ to

9.4×10^{-6} M when

$[\text{NH}_3] = 0.10$.

$$K_{\text{b}} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{[\text{NH}_4^+](9.4 \times 10^{-6})}{0.10} = 1.8 \times 10^{-5} \quad [\text{NH}_4^+] = 0.19 \text{ M}$$

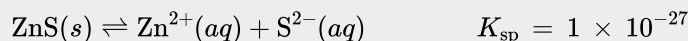
Equation:

When $[\text{NH}_4^+]$ equals 0.19 M, $[\text{OH}^-]$ will be 9.4×10^{-6} M. Any $[\text{NH}_4^+]$ greater than 0.19 M will reduce $[\text{OH}^-]$ below 9.4×10^{-6} M and prevent the formation of $\text{Mg}(\text{OH})_2$.

Check Your Learning

Consider the two equilibria:

Equation:



Equation:



and calculate the concentration of hydronium ion required to prevent the precipitation of ZnS in a solution that is 0.050 M in Zn^{2+} and saturated with H_2S (0.10 M H_2S).

Note:

Answer:

$[\text{H}_3\text{O}^+] > 0.2 \text{ M}$

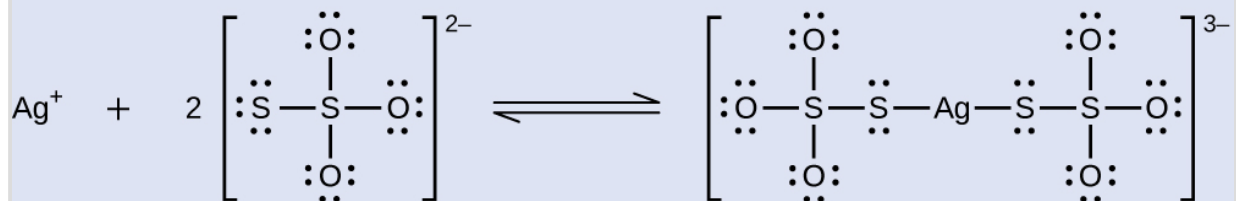
($[\text{S}^{2-}]$ is less than 2×10^{-26} M and precipitation of ZnS does not occur.)

Therefore, precise calculations of the solubility of solids from the solubility product are limited to cases in which the only significant reaction occurring when the solid dissolves is the formation of its ions.

Example:

Multiple Equilibria

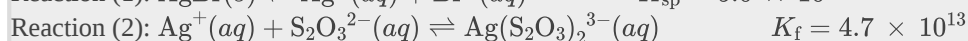
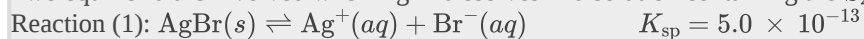
Unexposed silver halides are removed from photographic film when they react with sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$, called hypo) to form the complex ion $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ ($K_{\text{f}} = 4.7 \times 10^{13}$). The reaction with silver bromide is:



What mass of $\text{Na}_2\text{S}_2\text{O}_3$ is required to prepare 1.00 L of a solution that will dissolve 1.00 g of AgBr by the formation of $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$?

Solution

Two equilibria are involved when AgBr dissolves in a solution containing the $\text{S}_2\text{O}_3^{2-}$ ion:



In order for 1.00 g of AgBr to dissolve, the $[\text{Ag}^+]$ in the solution that results must be low enough for Q for Reaction (1) to be smaller than K_{sp} for this reaction. We reduce $[\text{Ag}^+]$ by adding $\text{S}_2\text{O}_3^{2-}$ and thus cause Reaction (2) to shift to the right. We need the following steps to determine what mass of $\text{Na}_2\text{S}_2\text{O}_3$ is needed to provide the necessary $\text{S}_2\text{O}_3^{2-}$.

Equation:

We calculate the $[\text{Br}^-]$ produced by the complete dissolution of 1.00 g of AgBr ($5.33 \times 10^{-3} \text{ mol AgBr}$) in 1.00 L of solution:

$$[\text{Br}^-] = 5.33 \times 10^{-3} M$$

Equation:

We use $[\text{Br}^-]$ and K_{sp} to determine the maximum possible concentration of Ag^+ that can be present without causing reprecipitation of AgBr :

$$[\text{Ag}^+] = 9.4 \times 10^{-11} M$$

Equation:

We determine $\text{Ag}^+ + 2\text{S}_2\text{O}_3^{2-} \rightleftharpoons \text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$

the $[\text{S}_2\text{O}_3^{2-}]$ required to make

$$[\text{Ag}^+] = 9.4 \times 10^{-11} M \text{ after the remaining}$$

Ag^+ ion has reacted with $\text{S}_2\text{O}_3^{2-}$ according to the equation:

Equation:

We determine the total number of moles of $\text{S}_2\text{O}_3^{2-}$ that must be added to the solution. This equals the amount that reacts with Ag^+ to form $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$

$$2 \times (5.33 \times 10^{-3} \text{ mol S}_2\text{O}_3^{2-}) + 1.1 \times 10^{-3} \text{ mol S}_2\text{O}_3^{2-} = 1.18 \times 10^{-2} \text{ mol S}_2\text{O}_3^{2-}$$

Equation:

Because $K_f = 4.7 \times 10^{13}$, $5.33 \times 10^{-3} \text{ mol}$ of AgBr dissolves:

plus the amount of free $\text{S}_2\text{O}_3^{2-}$ in solution at equilibrium. To form 5.33×10^{-3} mol of $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ requires $2 \times (5.33 \times 10^{-3})$ mol of $\text{S}_2\text{O}_3^{2-}$. In addition, 1.1×10^{-3} mol of unreacted $\text{S}_2\text{O}_3^{2-}$ is present (Step 3). Thus, the total amount of $\text{S}_2\text{O}_3^{2-}$ that must be added is:

Equation:

We determine the mass of $\text{Na}_2\text{S}_2\text{O}_3$ required to give 1.18×10^{-2} mol $\text{S}_2\text{O}_3^{2-}$ using the molar mass of $\text{Na}_2\text{S}_2\text{O}_3$:

$$1.18 \times 10^{-2} \text{ mol } \text{S}_2\text{O}_3^{2-} \times \frac{158.1 \text{ g } \text{Na}_2\text{S}_2\text{O}_3}{1 \text{ mol } \text{Na}_2\text{S}_2\text{O}_3} = 1.9 \text{ g } \text{Na}_2\text{S}_2\text{O}_3$$

Thus, 1.00 L of a solution prepared from 1.9 g $\text{Na}_2\text{S}_2\text{O}_3$ dissolves 1.0 g of AgBr.

Check Your Learning

$\text{AgCl}(s)$, silver chloride, is well known to have a very low solubility: $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$, $K_{\text{sp}} = 1.6 \times 10^{-10}$. Adding ammonia significantly increases the solubility of AgCl because a complex ion is formed: $\text{Ag}^+(aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(aq)$, $K_{\text{f}} = 1.7 \times 10^7$. What mass of NH_3 is required to prepare 1.00 L of solution that will dissolve 2.00 g of AgCl by formation of $\text{Ag}(\text{NH}_3)_2^+$?

Note:

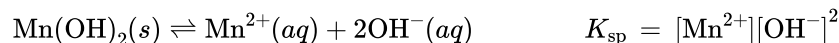
Answer:

1.00 L of a solution prepared with 4.81 g NH_3 dissolves 2.0 g of AgCl.

Dissolution versus Weak Electrolyte Formation

We can determine how to shift the concentration of ions in the equilibrium between a slightly soluble solid and a solution of its ions by applying Le Châtelier's principle. For example, one way to control the concentration of manganese(II) ion, Mn^{2+} , in a solution is to adjust the pH of the solution and, consequently, to manipulate the equilibrium between the slightly soluble solid manganese(II) hydroxide, manganese(II) ion, and hydroxide ion:

Equation:



This could be important to a laundromat because clothing washed in water that has a manganese concentration exceeding 0.1 mg per liter may be stained by the manganese. We can reduce the concentration of manganese by increasing the concentration of hydroxide ion. We could add, for example, a small amount of NaOH or some other base such as the silicates found in many laundry detergents. As the concentration of OH^- ion increases, the equilibrium responds by shifting to the left and reducing the concentration of Mn^{2+} ion while increasing the amount of solid $\text{Mn}(\text{OH})_2$ in the equilibrium mixture, as predicted by Le Châtelier's principle.

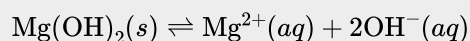
Example:**Solubility Equilibrium of a Slightly Soluble Solid**

What is the effect on the amount of solid $\text{Mg}(\text{OH})_2$ that dissolves and the concentrations of Mg^{2+} and OH^- when each of the following are added to a mixture of solid $\text{Mg}(\text{OH})_2$ in water at equilibrium?

- (a) MgCl_2
- (b) KOH
- (c) an acid
- (d) NaNO_3
- (e) $\text{Mg}(\text{OH})_2$

Solution

The equilibrium among solid $\text{Mg}(\text{OH})_2$ and a solution of Mg^{2+} and OH^- is:

Equation:

(a) The reaction shifts to the left to relieve the stress produced by the additional Mg^{2+} ion, in accordance with Le Châtelier's principle. In quantitative terms, the added Mg^{2+} causes the reaction quotient to be larger than the solubility product ($Q > K_{\text{sp}}$), and $\text{Mg}(\text{OH})_2$ forms until the reaction quotient again equals K_{sp} . At the new equilibrium, $[\text{OH}^-]$ is less and $[\text{Mg}^{2+}]$ is greater than in the solution of $\text{Mg}(\text{OH})_2$ in pure water. More solid $\text{Mg}(\text{OH})_2$ is present.

(b) The reaction shifts to the left to relieve the stress of the additional OH^- ion. $\text{Mg}(\text{OH})_2$ forms until the reaction quotient again equals K_{sp} . At the new equilibrium, $[\text{OH}^-]$ is greater and $[\text{Mg}^{2+}]$ is less than in the solution of $\text{Mg}(\text{OH})_2$ in pure water. More solid $\text{Mg}(\text{OH})_2$ is present.

(c) The concentration of OH^- is reduced as the OH^- reacts with the acid. The reaction shifts to the right to relieve the stress of less OH^- ion. In quantitative terms, the decrease in the OH^- concentration causes the reaction quotient to be smaller than the solubility product ($Q < K_{\text{sp}}$), and additional $\text{Mg}(\text{OH})_2$ dissolves until the reaction quotient again equals K_{sp} . At the new equilibrium, $[\text{OH}^-]$ is less and $[\text{Mg}^{2+}]$ is greater than in the solution of $\text{Mg}(\text{OH})_2$ in pure water. More $\text{Mg}(\text{OH})_2$ is dissolved.

(d) NaNO_3 contains none of the species involved in the equilibrium, so we should expect that it has no appreciable effect on the concentrations of Mg^{2+} and OH^- . (As we have seen previously, dissolved salts change the activities of the ions of an electrolyte. However, the salt effect is generally small, and we shall neglect the slight errors that may result from it.)

(e) The addition of solid $\text{Mg}(\text{OH})_2$ has no effect on the solubility of $\text{Mg}(\text{OH})_2$ or on the concentration of Mg^{2+} and OH^- . The concentration of $\text{Mg}(\text{OH})_2$ does not appear in the equation for the reaction quotient:

Equation:

$$Q = [\text{Mg}^{2+}][\text{OH}^-]^2$$

Thus, changing the amount of solid magnesium hydroxide in the mixture has no effect on the value of Q , and no shift is required to restore Q to the value of the equilibrium constant.

Check Your Learning

What is the effect on the amount of solid NiCO_3 that dissolves and the concentrations of Ni^{2+} and CO_3^{2-} when each of the following are added to a mixture of the slightly soluble solid NiCO_3 and water at equilibrium?

- (a) $\text{Ni}(\text{NO}_3)_2$
- (b) KClO_4
- (c) NiCO_3
- (d) K_2CO_3
- (e) HNO_3 (reacts with carbonate giving HCO_3^- or H_2O and CO_2)

Note:**Answer:**

(a) mass of $\text{NiCO}_3(s)$ increases, $[\text{Ni}^{2+}]$ increases, $[\text{CO}_3^{2-}]$ decreases; (b) no appreciable effect; (c) no effect except to increase the amount of solid NiCO_3 ; (d) mass of $\text{NiCO}_3(s)$ increases, $[\text{Ni}^{2+}]$ decreases, $[\text{CO}_3^{2-}]$ increases; (e) mass of $\text{NiCO}_3(s)$ decreases, $[\text{Ni}^{2+}]$ increases, $[\text{CO}_3^{2-}]$ decreases

Key Concepts and Summary

Several systems we encounter consist of multiple equilibria, systems where two or more equilibria processes are occurring simultaneously. Some common examples include acid rain, fluoridation, and dissolution of carbon dioxide in sea water. When looking at these systems, we need to consider each equilibrium separately and then combine the individual equilibrium constants into one solubility product or reaction quotient expression using the tools from the first equilibrium chapter. Le Châtelier's principle also must be considered, as each reaction in a multiple equilibria system will shift toward reactants or products based on what is added to the initial reaction and how it affects each subsequent equilibrium reaction.

Chemistry End of Chapter Exercises

Exercise:

Problem:

A saturated solution of a slightly soluble electrolyte in contact with some of the solid electrolyte is said to be a system in equilibrium. Explain. Why is such a system called a heterogeneous equilibrium?

Exercise:

Problem: Calculate the equilibrium concentration of Ni^{2+} in a 1.0-*M* solution $[\text{Ni}(\text{NH}_3)_6](\text{NO}_3)_2$.

Solution:

0.014 *M*

Exercise:

Problem: Calculate the equilibrium concentration of Zn^{2+} in a 0.30-*M* solution of $\text{Zn}(\text{CN})_4^{2-}$.

Exercise:

Problem:

Calculate the equilibrium concentration of Cu^{2+} in a solution initially with 0.050 *M* Cu^{2+} and 1.00 *M* NH_3 .

Solution:

7.2×10^{-15} *M*

Exercise:

Problem:

Calculate the equilibrium concentration of Zn^{2+} in a solution initially with 0.150 *M* Zn^{2+} and 2.50 *M* CN^- .

Exercise:

Problem:

Calculate the Fe^{3+} equilibrium concentration when 0.0888 mole of $\text{K}_3[\text{Fe}(\text{CN})_6]$ is added to a solution with 0.0.00010 *M* CN^- .

Solution:

$$4.4 \times 10^{-22} M$$

Exercise:**Problem:**

Calculate the Co^{2+} equilibrium concentration when 0.100 mole of $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_2$ is added to a solution with 0.025 M NH_3 . Assume the volume is 1.00 L.

Exercise:**Problem:**

The equilibrium constant for the reaction $\text{Hg}^{2+}(aq) + 2\text{Cl}^-(aq) \rightleftharpoons \text{HgCl}_2(aq)$ is 1.6×10^{13} . Is HgCl_2 a strong electrolyte or a weak electrolyte? What are the concentrations of Hg^{2+} and Cl^- in a 0.015-M solution of HgCl_2 ?

Solution:

$6.2 \times 10^{-6} M = [\text{Hg}^{2+}]$; $1.2 \times 10^{-5} M = [\text{Cl}^-]$; The substance is a weak electrolyte because very little of the initial 0.015 M HgCl_2 dissolved.

Exercise:**Problem:**

Calculate the molar solubility of $\text{Sn}(\text{OH})_2$ in a buffer solution containing equal concentrations of NH_3 and NH_4^+ .

Exercise:**Problem:**

Calculate the molar solubility of $\text{Al}(\text{OH})_3$ in a buffer solution with 0.100 M NH_3 and 0.400 M NH_4^+ .

Solution:

$[\text{OH}^-] = 4.5 \times 10^{-5}$; $[\text{Al}^{3+}] = 2.2 \times 10^{-20}$ (molar solubility)

Exercise:

Problem: What is the molar solubility of CaF_2 in a 0.100-M solution of HF? K_a for HF = 7.2×10^{-4} .

Exercise:**Problem:**

What is the molar solubility of BaSO_4 in a 0.250-M solution of NaHSO_4 ? K_a for $\text{HSO}_4^- = 1.2 \times 10^{-2}$.

Solution:

$[\text{SO}_4^{2-}] = 0.049 M$
 $[\text{Ba}^{2+}] = 4.7 \times 10^{-7}$ (molar solubility)

Exercise:

Problem: What is the molar solubility of $\text{Tl}(\text{OH})_3$ in a 0.10-M solution of NH_3 ?

Exercise:

Problem: What is the molar solubility of $\text{Pb}(\text{OH})_2$ in a 0.138-M solution of CH_3NH_2 ?

Solution:

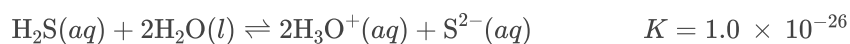
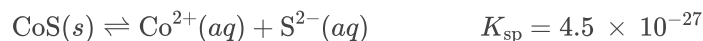
$$[\text{OH}^-] = 7.6 \times 10^{-3} \text{ M}$$

$$[\text{Pb}^{2+}] = 2.1 \times 10^{-11} \text{ (molar solubility)}$$

Exercise:

Problem:

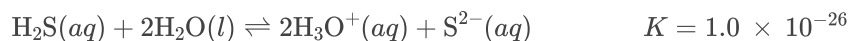
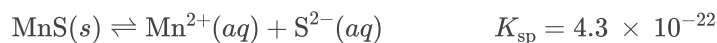
A solution of 0.075 M CoBr₂ is saturated with H₂S ([H₂S] = 0.10 M). What is the minimum pH at which CoS begins to precipitate?



Exercise:

Problem:

A 0.125-M solution of Mn(NO₃)₂ is saturated with H₂S ([H₂S] = 0.10 M). At what pH does MnS begin to precipitate?



Solution:

7.66

Exercise:

Problem: Calculate the molar solubility of BaF₂ in a buffer solution containing 0.20 M HF and 0.20 M NaF.

Exercise:

Problem:

Calculate the molar solubility of CdCO₃ in a buffer solution containing 0.115 M Na₂CO₃ and 0.120 M NaHCO₃

Solution:

$$[\text{CO}_3^{2-}] = 0.116 \text{ M}$$

$$[\text{Cd}^{2+}] = 4.5 \times 10^{-11} \text{ M}$$

Exercise:

Problem: To a 0.10-M solution of Pb(NO₃)₂ is added enough HF(g) to make [HF] = 0.10 M.

(a) Does PbF₂ precipitate from this solution? Show the calculations that support your conclusion.

(b) What is the minimum pH at which PbF₂ precipitates?

Exercise:

Problem:

Calculate the concentration of Cd²⁺ resulting from the dissolution of CdCO₃ in a solution that is 0.250 M in CH₃CO₂H, 0.375 M in NaCH₃CO₂, and 0.010 M in H₂CO₃.

Solution:

$$3.1 \times 10^{-3} M$$

Exercise:

Problem: Both AgCl and AgI dissolve in NH_3 .

(a) What mass of AgI dissolves in 1.0 L of 1.0 M NH_3 ?

(b) What mass of AgCl dissolves in 1.0 L of 1.0 M NH_3 ?

Exercise:

Problem:

Calculate the volume of 1.50 M $\text{CH}_3\text{CO}_2\text{H}$ required to dissolve a precipitate composed of 350 mg each of CaCO_3 , SrCO_3 , and BaCO_3 .

Solution:

0.0102 L (10.2 mL)

Exercise:

Problem:

Even though $\text{Ca}(\text{OH})_2$ is an inexpensive base, its limited solubility restricts its use. What is the pH of a saturated solution of $\text{Ca}(\text{OH})_2$?

Exercise:

Problem:

What mass of NaCN must be added to 1 L of 0.010 M $\text{Mg}(\text{NO}_3)_2$ in order to produce the first trace of $\text{Mg}(\text{OH})_2$?

Solution:

0.0036 g

Exercise:

Problem:

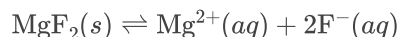
Magnesium hydroxide and magnesium citrate function as mild laxatives when they reach the small intestine. Why do magnesium hydroxide and magnesium citrate, two very different substances, have the same effect in your small intestine. (Hint: The contents of the small intestine are basic.)

Exercise:

Problem:

The following question is taken from a Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

Solve the following problem:



In a saturated solution of MgF_2 at 18 °C, the concentration of Mg^{2+} is $1.21 \times 10^{-3} M$. The equilibrium is represented by the preceding equation.

(a) Write the expression for the solubility-product constant, K_{sp} , and calculate its value at 18 °C.

(b) Calculate the equilibrium concentration of Mg^{2+} in 1.000 L of saturated MgF_2 solution at 18 °C to which 0.100 mol of solid KF has been added. The KF dissolves completely. Assume the volume change is negligible.

(c) Predict whether a precipitate of MgF_2 will form when 100.0 mL of a $3.00 \times 10^{-3} M$ solution of $\text{Mg}(\text{NO}_3)_2$ is mixed with 200.0 mL of a $2.00 \times 10^{-3} M$ solution of NaF at 18 °C. Show the calculations to support your prediction.

(d) At 27 °C the concentration of Mg^{2+} in a saturated solution of MgF_2 is $1.17 \times 10^{-3} M$. Is the dissolving of MgF_2 in water an endothermic or an exothermic process? Give an explanation to support your conclusion.

Solution:

(a) $K_{\text{sp}} = [\text{Mg}^{2+}][\text{F}^-]^2 = (1.21 \times 10^{-3})(2 \times 1.21 \times 10^{-3})^2 = 7.09 \times 10^{-9}$; (b) $7.09 \times 10^{-7} M$

(c) Determine the concentration of Mg^{2+} and F^- that will be present in the final volume. Compare the value of the ion product $[\text{Mg}^{2+}][\text{F}^-]^2$ with K_{sp} . If this value is larger than K_{sp} , precipitation will occur.

$0.1000 \text{ L} \times 3.00 \times 10^{-3} M \text{ Mg}(\text{NO}_3)_2 = 0.3000 \text{ L} \times M \text{ Mg}(\text{NO}_3)_2$

$M \text{ Mg}(\text{NO}_3)_2 = 1.00 \times 10^{-3} M$

$0.2000 \text{ L} \times 2.00 \times 10^{-3} M \text{ NaF} = 0.3000 \text{ L} \times M \text{ NaF}$

$M \text{ NaF} = 1.33 \times 10^{-3} M$

ion product = $(1.00 \times 10^{-3})(1.33 \times 10^{-3})^2 = 1.77 \times 10^{-9}$

This value is smaller than K_{sp} , so no precipitation will occur.

(d) MgF_2 is less soluble at 27 °C than at 18 °C. Because added heat acts like an added reagent, when it appears on the product side, the Le Châtelier's principle states that the equilibrium will shift to the reactants' side to counter the stress. Consequently, less reagent will dissolve. This situation is found in our case.

Therefore, the reaction is exothermic.

Exercise:

Problem:

Which of the following compounds, when dissolved in a 0.01-M solution of HClO_4 , has a solubility greater than in pure water: CuCl, CaCO_3 , MnS, PbBr_2 , CaF_2 ? Explain your answer.

Exercise:

Problem:

Which of the following compounds, when dissolved in a 0.01-M solution of HClO_4 , has a solubility greater than in pure water: AgBr, BaF_2 , $\text{Ca}_3(\text{PO}_4)_2$, ZnS, PbI_2 ? Explain your answer.

Solution:

BaF_2 , $\text{Ca}_3(\text{PO}_4)_2$, ZnS; each is a salt of a weak acid, and the $[\text{H}_3\text{O}^+]$ from perchloric acid reduces the equilibrium concentration of the anion, thereby increasing the concentration of the cations

Exercise:

Problem:

What is the effect on the amount of solid $\text{Mg}(\text{OH})_2$ that dissolves and the concentrations of Mg^{2+} and OH^- when each of the following are added to a mixture of solid $\text{Mg}(\text{OH})_2$ and water at equilibrium?

(a) MgCl_2

(b) KOH

(c) HClO_4

(d) NaNO_3

(e) $\text{Mg}(\text{OH})_2$

Exercise:

Problem:

What is the effect on the amount of CaHPO_4 that dissolves and the concentrations of Ca^{2+} and HPO_4^- when each of the following are added to a mixture of solid CaHPO_4 and water at equilibrium?

(a) CaCl_2

(b) HCl

(c) KClO_4

(d) NaOH

(e) CaHPO_4

Solution:

Effect on amount of solid CaHPO_4 , $[\text{Ca}^{2+}]$, $[\text{OH}^-]$: (a) increase, increase, decrease; (b) decrease, increase, decrease; (c) no effect, no effect, no effect; (d) decrease, increase, decrease; (e) increase, no effect, no effect

Exercise:

Problem:

Identify all chemical species present in an aqueous solution of $\text{Ca}_3(\text{PO}_4)_2$ and list these species in decreasing order of their concentrations. (Hint: Remember that the PO_4^{3-} ion is a weak base.)

Exercise:

Problem:

A volume of 50 mL of 1.8 M NH_3 is mixed with an equal volume of a solution containing 0.95 g of MgCl_2 . What mass of NH_4Cl must be added to the resulting solution to prevent the precipitation of $\text{Mg}(\text{OH})_2$?

Solution:

9.2 g

Glossary

multiple equilibrium




system characterized by more than one state of balance between a slightly soluble ionic solid and an aqueous solution of ions working simultaneously

Periodic Table of the Elements

Period	Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1		1 H 1.008 hydrogen																	2 He 4.003 helium
2		3 Li 6.94 lithium	4 Be 9.012 beryllium																
3		11 Na 22.99 sodium	12 Mg 24.31 magnesium											13 Al 26.98 aluminum	14 Si 28.09 silicon	15 P 30.97 phosphorus	16 S 32.06 sulfur	17 Cl 35.45 chlorine	18 Ar 39.95 argon
4		19 K 39.10 potassium	20 Ca 40.08 calcium	21 Sc 44.96 scandium	22 Ti 47.87 titanium	23 V 50.94 vanadium	24 Cr 52.00 chromium	25 Mn 54.94 manganese	26 Fe 55.85 iron	27 Co 58.93 cobalt	28 Ni 58.69 nickel	29 Cu 63.55 copper	30 Zn 65.38 zinc	31 Ga 69.72 gallium	32 Ge 72.63 germanium	33 As 74.92 arsenic	34 Se 78.97 selenium	35 Br 79.90 bromine	36 Kr 83.80 krypton
5		37 Rb 85.47 rubidium	38 Sr 87.62 strontium	39 Y 88.91 yttrium	40 Zr 91.22 zirconium	41 Nb 92.91 niobium	42 Mo 95.95 molybdenum	43 Tc [97] technetium	44 Ru 101.1 ruthenium	45 Rh 102.9 rhodium	46 Pd 106.4 palladium	47 Ag 107.9 silver	48 Cd 112.4 cadmium	49 In 114.8 indium	50 Sn 118.7 tin	51 Sb 121.8 antimony	52 Te 127.6 tellurium	53 I 126.9 iodine	54 Xe 131.3 xenon
6		55 Cs 132.9 cesium	56 Ba 137.3 barium	57-71 La-Lu *	72 Hf 178.5 hafnium	73 Ta 180.9 tantalum	74 W 183.8 tungsten	75 Re 186.2 rhenium	76 Os 190.2 osmium	77 Ir 192.2 iridium	78 Pt 195.1 platinum	79 Au 197.0 gold	80 Hg 200.6 mercury	81 Tl 204.4 thallium	82 Pb 207.2 lead	83 Bi 209.0 bismuth	84 Po [209] polonium	85 At [210] astatine	86 Rn [222] radon
7		87 Fr [223] francium	88 Ra [226] radium	89-103 Ac-Lr **	104 Rf [267] rutherfordium	105 Db [270] dubnium	106 Sg [271] seaborgium	107 Bh [270] bohrium	108 Hs [277] hassium	109 Mt [276] meitnerium	110 Ds [281] darmstadtium	111 Rg [282] roentgenium	112 Cn [285] copernicium	113 Uut [285] ununtrium	114 Fl [289] flerovium	115 Uup [288] ununpentium	116 Lv [293] livermorium	117 Uus [294] ununseptium	118 Uuo [294] ununoctium
					57 La 138.9 lanthanum	58 Ce 140.1 cerium	59 Pr 140.9 praseodymium	60 Nd 144.2 neodymium	61 Pm [145] promethium	62 Sm 150.4 samarium	63 Eu 152.0 europium	64 Gd 157.3 gadolinium	65 Tb 158.9 terbium	66 Dy 162.5 dysprosium	67 Ho 164.9 holmium	68 Er 167.3 erbium	69 Tm 168.9 thulium	70 Yb 173.1 ytterbium	71 Lu 175.0 lutetium
					89 Ac [227] actinium	90 Th 232.0 thorium	91 Pa 231.0 protactinium	92 U 238.0 uranium	93 Np [237] neptunium	94 Pu [244] plutonium	95 Am [243] americium	96 Cm [247] curium	97 Bk [247] berkelium	98 Cf [251] californium	99 Es [252] einsteinium	100 Fm [257] fermium	101 Md [258] mendelevium	102 No [259] nobelium	103 Lr [262] lawrencium

The diagram shows a single element box from the periodic table for Hydrogen. The box is light blue with a thin black border. Inside the box, the atomic number '1' is at the top left, the symbol 'H' is in the center, the atomic mass '1.008' is below the symbol, and the name 'hydrogen' is at the bottom. Four arrows point from labels outside the box to these specific elements: 'Atomic number' points to '1', 'Symbol' points to 'H', 'Atomic mass' points to '1.008', and 'Name' points to 'hydrogen'.

Atomic number	1	Symbol	H
		Atomic mass	1.008
Name	hydrogen		

Color Code		
	Metal	Solid
	Metalloid	Liquid
	Nonmetal	Gas

Exponential Arithmetic

Exponential notation is used to express very large and very small numbers as a product of two numbers. The first number of the product, the *digit term*, is usually a number not less than 1 and not greater than 10. The second number of the product, the *exponential term*, is written as 10 with an exponent. Some examples of exponential notation are:

Equation:

$$\begin{aligned}1000 &= 1 \times 10^3 \\100 &= 1 \times 10^2 \\10 &= 1 \times 10^1 \\1 &= 1 \times 10^0 \\0.1 &= 1 \times 10^{-1} \\0.001 &= 1 \times 10^{-3} \\2386 &= 2.386 \times 1000 = 2.386 \times 10^3 \\0.123 &= 1.23 \times 0.1 = 1.23 \times 10^{-1}\end{aligned}$$

The power (exponent) of 10 is equal to the number of places the decimal is shifted to give the digit number. The exponential method is particularly useful notation for every large and very small numbers. For example, $1,230,000,000 = 1.23 \times 10^9$, and $0.00000000036 = 3.6 \times 10^{-10}$.

Addition of Exponentials

Convert all numbers to the same power of 10, add the digit terms of the numbers, and if appropriate, convert the digit term back to a number between 1 and 10 by adjusting the exponential term.

Example:

Adding Exponentials

Add 5.00×10^{-5} and 3.00×10^{-3} .

Solution

Equation:

$$\begin{aligned} 3.00 \times 10^{-3} &= 300 \times 10^{-5} \\ (5.00 \times 10^{-5}) + (300 \times 10^{-5}) &= 305 \times 10^{-5} = 3.05 \times 10^{-3} \end{aligned}$$

Subtraction of Exponentials

Convert all numbers to the same power of 10, take the difference of the digit terms, and if appropriate, convert the digit term back to a number between 1 and 10 by adjusting the exponential term.

Example:

Subtracting Exponentials

Subtract 4.0×10^{-7} from 5.0×10^{-6} .

Solution

Equation:

$$\begin{aligned} 4.0 \times 10^{-7} &= 0.40 \times 10^{-6} \\ (5.0 \times 10^{-6}) - (0.40 \times 10^{-6}) &= 4.6 \times 10^{-6} \end{aligned}$$

Multiplication of Exponentials

Multiply the digit terms in the usual way and add the exponents of the exponential terms.

Example:

Multiplying Exponentials

Multiply 4.2×10^{-8} by 2.0×10^3 .

Solution

Equation:

$$(4.2 \times 10^{-8}) \times (2.0 \times 10^3) = (4.2 \times 2.0) \times 10^{(-8)+(3)} = 8.4 \times 10^{-5}$$

Division of Exponentials

Divide the digit term of the numerator by the digit term of the denominator and subtract the exponents of the exponential terms.

Example:

Dividing Exponentials

Divide 3.6×10^5 by 6.0×10^{-4} .

Solution

Equation:

$$\frac{3.6 \times 10^5}{6.0 \times 10^{-4}} = \left(\frac{3.6}{6.0} \right) \times 10^{(5)-(-4)} = 0.60 \times 10^{-1} = 6.0 \times 10^{-2}$$

Squaring of Exponentials

Square the digit term in the usual way and multiply the exponent of the exponential term by 2.

Example:

Squaring Exponentials

Square the number 4.0×10^{-6} .

Solution

Equation:

$$(4.0 \times 10^{-6})^2 = 4 \times 4 \times 10^{2 \times (-6)} = 16 \times 10^{-12} = 1.6 \times 10^{-11}$$

Cubing of Exponentials

Cube the digit term in the usual way and multiply the exponent of the exponential term by 3.

Example:**Cubing Exponentials**

Cube the number 2×10^4 .

Solution**Equation:**

$$(2 \times 10^4)^3 = 2 \times 2 \times 2 \times 10^{3 \times 4} = 8 \times 10^{12}$$

Taking Square Roots of Exponentials

If necessary, decrease or increase the exponential term so that the power of 10 is evenly divisible by 2. Extract the square root of the digit term and divide the exponential term by 2.

Example:**Finding the Square Root of Exponentials**

Find the square root of 1.6×10^{-7} .

Solution**Equation:**

$$1.6 \times 10^{-7} = 16 \times 10^{-8}$$

$$\sqrt{16 \times 10^{-8}} = \sqrt{16} \times \sqrt{10^{-8}} = \sqrt{16} \times 10^{-\frac{8}{2}} = 4.0 \times 10^{-4}$$

Significant Figures

A beekeeper reports that he has 525,341 bees. The last three figures of the number are obviously inaccurate, for during the time the keeper was counting the bees, some of them died and others hatched; this makes it quite difficult to determine the exact number of bees. It would have been more accurate if the beekeeper had reported the number 525,000. In other words, the last three figures are not significant, except to set the position of the decimal point. Their exact values have no meaning useful in this situation. In reporting any information as numbers, use only as many significant figures as the accuracy of the measurement warrants.

The importance of significant figures lies in their application to fundamental computation. In addition and subtraction, the sum or difference should contain as many digits to the right of the decimal as that in the least certain of the numbers used in the computation (indicated by underscoring in the following example).

Example:

Addition and Subtraction with Significant Figures

Add 4.383 g and 0.0023 g.

Solution

Equation:

$$\begin{array}{r} 4.\underline{383} \text{ g} \\ 0.00\underline{23} \text{ g} \\ \hline 4.38\underline{5} \text{ g} \end{array}$$

In multiplication and division, the product or quotient should contain no more digits than that in the factor containing the least number of significant figures.

Example:

Multiplication and Division with Significant Figures

Multiply 0.6238 by 6.6.

Solution

Equation:

$$0.6238 \times 6.6 = 4.1$$

When rounding numbers, increase the retained digit by 1 if it is followed by a number larger than 5 (“round up”). Do not change the retained digit if the digits that follow are less than 5 (“round down”). If the retained digit is followed by 5, round up if the retained digit is odd, or round down if it is even (after rounding, the retained digit will thus always be even).

The Use of Logarithms and Exponential Numbers

The common logarithm of a number (log) is the power to which 10 must be raised to equal that number. For example, the common logarithm of 100 is 2, because 10 must be raised to the second power to equal 100. Additional examples follow.

Logarithms and Exponential Numbers		
Number	Number Expressed Exponentially	Common Logarithm

Logarithms and Exponential Numbers		
Number	Number Expressed Exponentially	Common Logarithm
1000	10^3	3
10	10^1	1
1	10^0	0
0.1	10^{-1}	-1
0.001	10^{-3}	-3

What is the common logarithm of 60? Because 60 lies between 10 and 100, which have logarithms of 1 and 2, respectively, the logarithm of 60 is 1.7782; that is,

Equation:

$$60 = 10^{1.7782}$$

The common logarithm of a number less than 1 has a negative value. The logarithm of 0.03918 is -1.4069, or

Equation:

$$0.03918 = 10^{-1.4069} = \frac{1}{10^{1.4069}}$$

To obtain the common logarithm of a number, use the *log* button on your calculator. To calculate a number from its logarithm, take the inverse log of the logarithm, or calculate 10^x (where x is the logarithm of the number).

The natural logarithm of a number (\ln) is the power to which e must be raised to equal the number; e is the constant 2.7182818. For example, the natural logarithm of 10 is 2.303; that is,

Equation:

$$10 = e^{2.303} = 2.7182818^{2.303}$$

To obtain the natural logarithm of a number, use the *ln* button on your calculator. To calculate a number from its natural logarithm, enter the natural logarithm and take the inverse ln of the natural logarithm, or calculate e^x (where x is the natural logarithm of the number).

Logarithms are exponents; thus, operations involving logarithms follow the same rules as operations involving exponents.

1. The logarithm of a product of two numbers is the sum of the logarithms of the two numbers.

Equation:

$$\log xy = \log x + \log y, \text{ and } \ln xy = \ln x + \ln y$$

2. The logarithm of the number resulting from the division of two numbers is the difference between the logarithms of the two numbers.

Equation:

$$\log \frac{x}{y} = \log x - \log y, \text{ and } \ln \frac{x}{y} = \ln x - \ln y$$

3. The logarithm of a number raised to an exponent is the product of the exponent and the logarithm of the number.

Equation:

$$\log x^n = n \log x \text{ and } \ln x^n = n \ln x$$

The Solution of Quadratic Equations

Mathematical functions of this form are known as second-order polynomials or, more commonly, quadratic functions.

Equation:

$$ax^2 + bx + c = 0$$

The solution or roots for any quadratic equation can be calculated using the following formula:

Equation:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Example:

Solving Quadratic Equations

Solve the quadratic equation $3x^2 + 13x - 10 = 0$.

Solution

Substituting the values $a = 3$, $b = 13$, $c = -10$ in the formula, we obtain

Equation:

$$x = \frac{-13 \pm \sqrt{(13)^2 - 4 \times 3 \times (-10)}}{2 \times 3}$$

Equation:

$$x = \frac{-13 \pm \sqrt{169 + 120}}{6} = \frac{-13 \pm \sqrt{289}}{6} = \frac{-13 \pm 17}{6}$$

The two roots are therefore

Equation:

$$x = \frac{-13 + 17}{6} = \frac{2}{3} \text{ and } x = \frac{-13 - 17}{6} = -5$$

Quadratic equations constructed on physical data always have real roots, and of these real roots, often only those having positive values are of any significance.

Two-Dimensional (x-y) Graphing

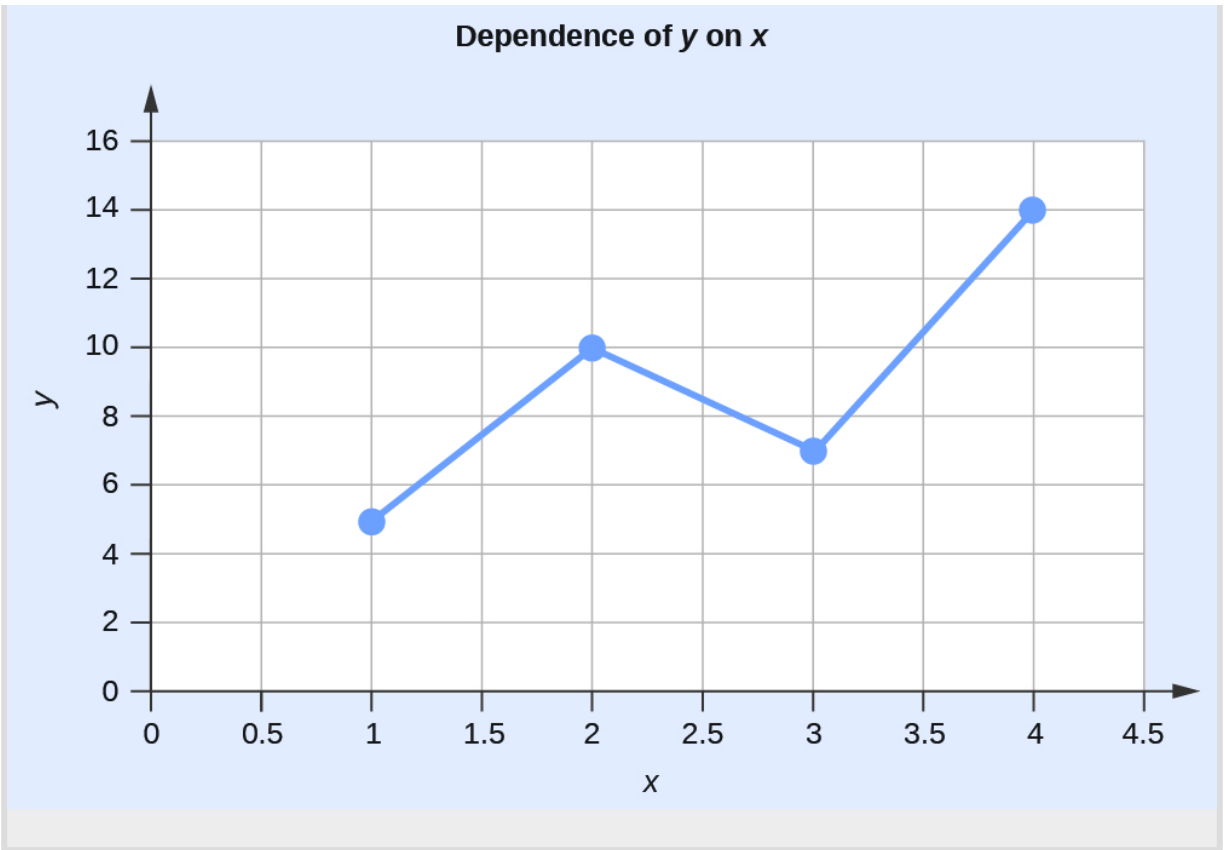
The relationship between any two properties of a system can be represented graphically by a two-dimensional data plot. Such a graph has two axes: a horizontal one corresponding to the independent variable, or the variable whose value is being controlled (x), and a vertical axis corresponding to the dependent variable, or the variable whose value is being observed or measured (y).

When the value of y is changing as a function of x (that is, different values of x correspond to different values of y), a graph of this change can be plotted or sketched. The graph can be produced by using specific values for (x,y) data pairs.

Example:
Graphing the Dependence of y on x

x	y
1	5
2	10
3	7
4	14

This table contains the following points: (1,5), (2,10), (3,7), and (4,14). Each of these points can be plotted on a graph and connected to produce a graphical representation of the dependence of y on x .



If the function that describes the dependence of y on x is known, it may be used to compute x,y data pairs that may subsequently be plotted.

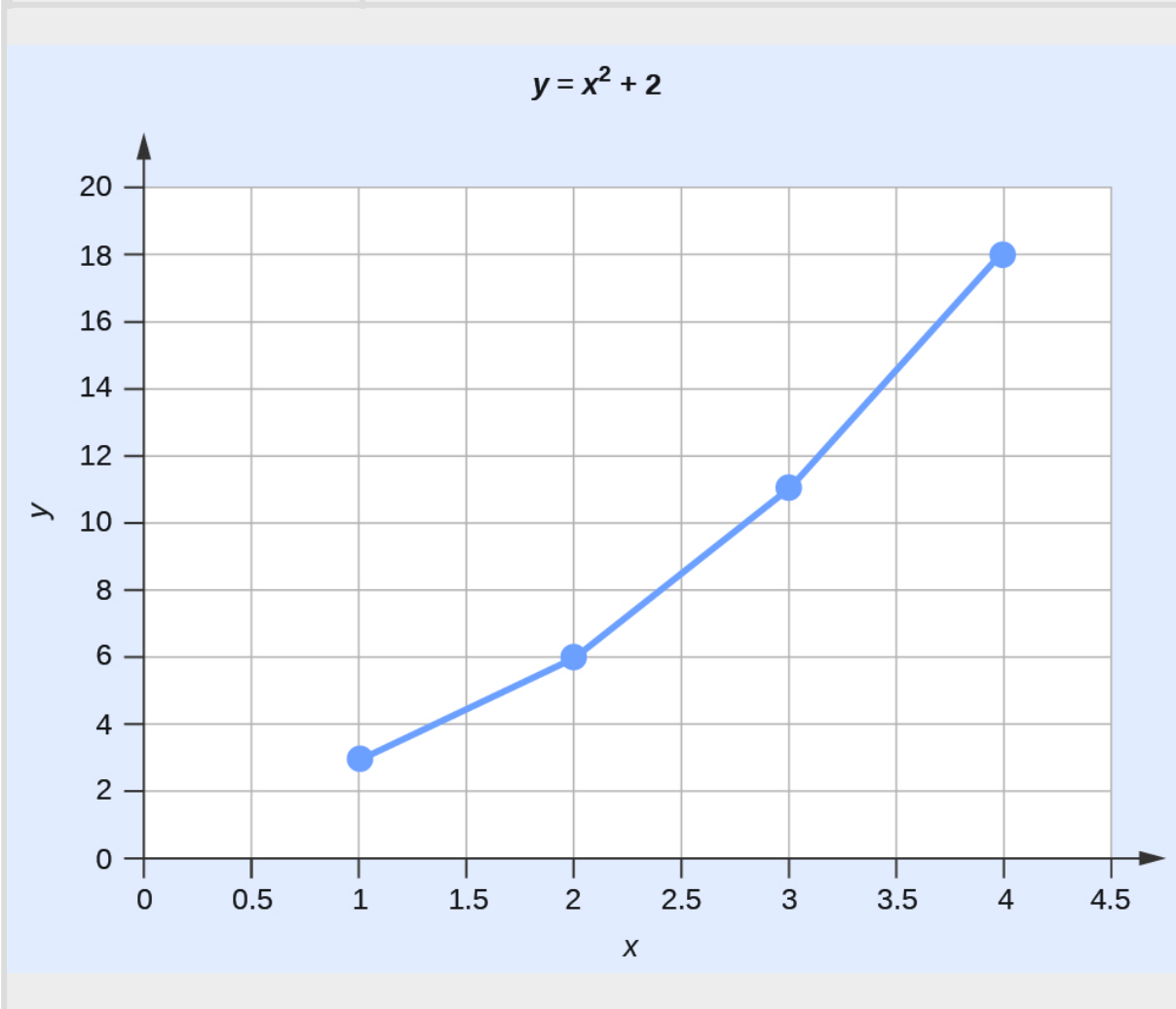
Example:

Plotting Data Pairs

If we know that $y = x^2 + 2$, we can produce a table of a few (x,y) values and then plot the line based on the data shown here.

x	$y = x^2 + 2$

x	$y = x^2 + 2$
1	3
2	6
3	11
4	18



Units and Conversion Factors

Units of Length			
meter (m)	= 39.37 inches (in.) = 1.094 yards (yd)	angstrom (Å)	= 10^{-8} cm (exact, definition) = 10^{-10} m (exact, definition)
centimeter (cm)	= 0.01 m (exact, definition)	yard (yd)	= 0.9144 m
millimeter (mm)	= 0.001 m (exact, definition)	inch (in.)	= 2.54 cm (exact, definition)
kilometer (km)	= 1000 m (exact, definition)	mile (US)	= 1.60934 km

Units of Volume

Units of Volume			
liter (L)	$= 0.001 \text{ m}^3$ (exact, definition) $= 1000 \text{ cm}^3$ (exact, definition) $= 1.057 \text{ (US) quarts}$	liquid quart (US)	$= 32 \text{ (US) liquid ounces (exact, definition)}$ $= 0.25 \text{ (US) gallon (exact, definition)}$ $= 0.9463 \text{ L}$
milliliter (mL)	$= 0.001 \text{ L}$ (exact, definition) $= 1 \text{ cm}^3$ (exact, definition)	dry quart	$= 1.1012 \text{ L}$
microliter (μL)	$= 10^{-6} \text{ L}$ (exact, definition) $= 10^{-3} \text{ cm}^3$ (exact, definition)	cubic foot (US)	$= 28.316 \text{ L}$

Units of Mass			
gram (g)	$= 0.001 \text{ kg}$ (exact, definition)	ounce (oz) (avoirdupois)	$= 28.35 \text{ g}$

Units of Mass			
milligram (mg)	= 0.001 g (exact, definition)	pound (lb) (avoirdupois)	= 0.4535924 kg
kilogram (kg)	= 1000 g (exact, definition) = 2.205 lb	ton (short)	=2000 lb (exact, definition) = 907.185 kg
ton (metric)	=1000 kg (exact, definition) = 2204.62 lb	ton (long)	= 2240 lb (exact, definition) = 1.016 metric ton

Units of Energy	
4.184 joule (J)	= 1 thermochemical calorie (cal)
1 thermochemical calorie (cal)	= 4.184×10^7 erg
erg	= 10^{-7} J (exact, definition)
electron-volt (eV)	= 1.60218×10^{-19} J = 23.061 kcal mol ⁻¹
liter·atmosphere	= 24.217 cal = 101.325 J (exact, definition)

Units of Energy	
nutritional calorie (Cal)	= 1000 cal (exact, definition) = 4184 J
British thermal unit (BTU)	= 1054.804 J [footnote] BTU is the amount of energy needed to heat one pound of water by one degree Fahrenheit. Therefore, the exact relationship of BTU to joules and other energy units depends on the temperature at which BTU is measured. 59 °F (15 °C) is the most widely used reference temperature for BTU definition in the United States. At this temperature, the conversion factor is the one provided in this table.

Units of Pressure	
torr	= 1 mm Hg (exact, definition)
pascal (Pa)	= N m ⁻² (exact, definition) = kg m ⁻¹ s ⁻² (exact, definition)
atmosphere (atm)	= 760 mm Hg (exact, definition) = 760 torr (exact, definition) = 101,325 N m ⁻² (exact, definition) = 101,325 Pa (exact, definition)
bar	= 10 ⁵ Pa (exact, definition) = 10 ⁵ kg m ⁻¹ s ⁻² (exact, definition)

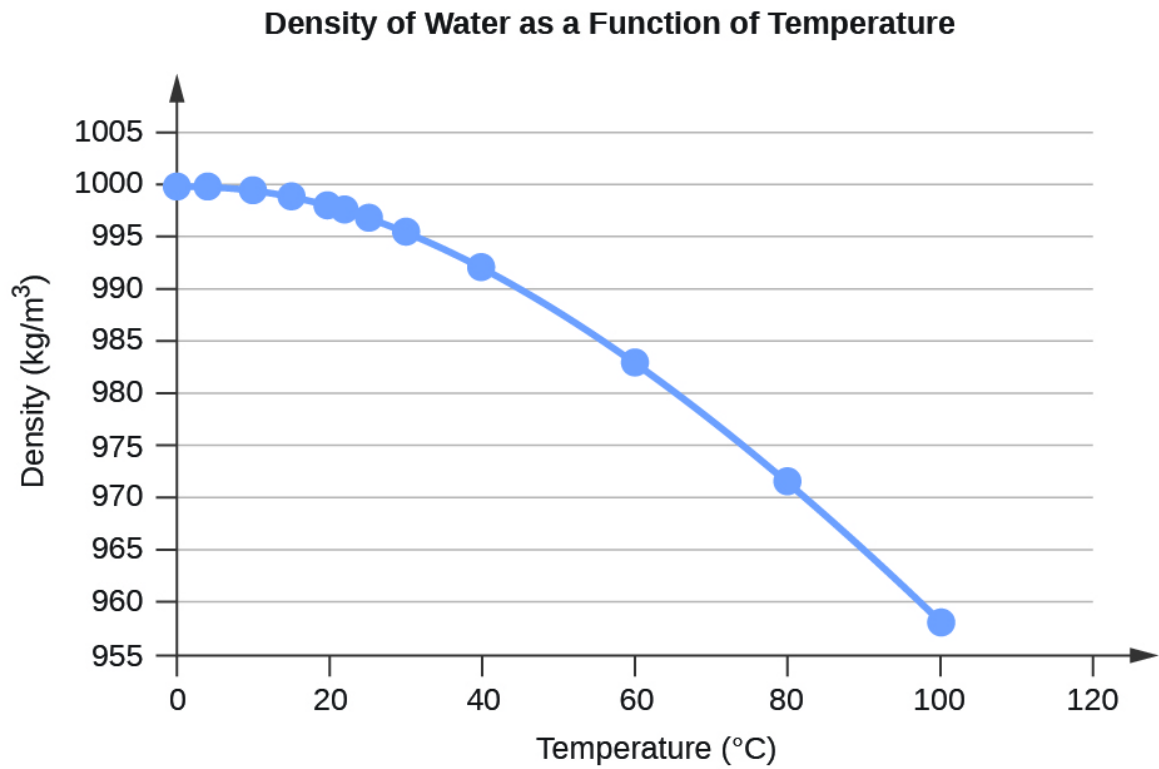
Fundamental Physical Constants

Fundamental Physical Constants	
Name and Symbol	Value
atomic mass unit (amu)	$1.6605402 \times 10^{-27} \text{ kg}$
Avogadro's number	$6.0221367 \times 10^{23} \text{ mol}^{-1}$
Boltzmann's constant (k)	$1.380658 \times 10^{-23} \text{ J K}^{-1}$
charge-to-mass ratio for electron (e/m_e)	$1.75881962 \times 10^{11} \text{ C kg}^{-1}$
electron charge (e)	$1.60217733 \times 10^{-19} \text{ C}$
electron rest mass (m_e)	$9.1093897 \times 10^{-31} \text{ kg}$
Faraday's constant (F)	$9.6485309 \times 10^4 \text{ C mol}^{-1}$
gas constant (R)	$8.205784 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1} = 8.314510 \text{ J mol}^{-1} \text{ K}^{-1}$
molar volume of an ideal gas, 1 atm, 0 °C	$22.41409 \text{ L mol}^{-1}$
molar volume of an ideal gas, 1 bar, 0 °C	$22.71108 \text{ L mol}^{-1}$
neutron rest mass (m_n)	$1.6749274 \times 10^{-27} \text{ kg}$

Fundamental Physical Constants	
Name and Symbol	Value
Planck's constant (h)	$6.6260755 \times 10^{-34} \text{ J s}$
proton rest mass (m_p)	$1.6726231 \times 10^{-27} \text{ kg}$
Rydberg constant (R)	$1.0973731534 \times 10^7 \text{ m}^{-1} =$ $2.1798736 \times 10^{-18} \text{ J}$
speed of light (in vacuum) (c)	$2.99792458 \times 10^8 \text{ m s}^{-1}$

Water Properties

Water Density (kg/m ³) at Different Temperatures (°C)	
Temperature ^{footnote} Data for t < 0 °C are for supercooled water	Density
0	999.8395
4	999.9720 (density maximum)
10	999.7026
15	999.1026
20	998.2071
22	997.7735
25	997.0479
30	995.6502
40	992.2
60	983.2
80	971.8
100	958.4

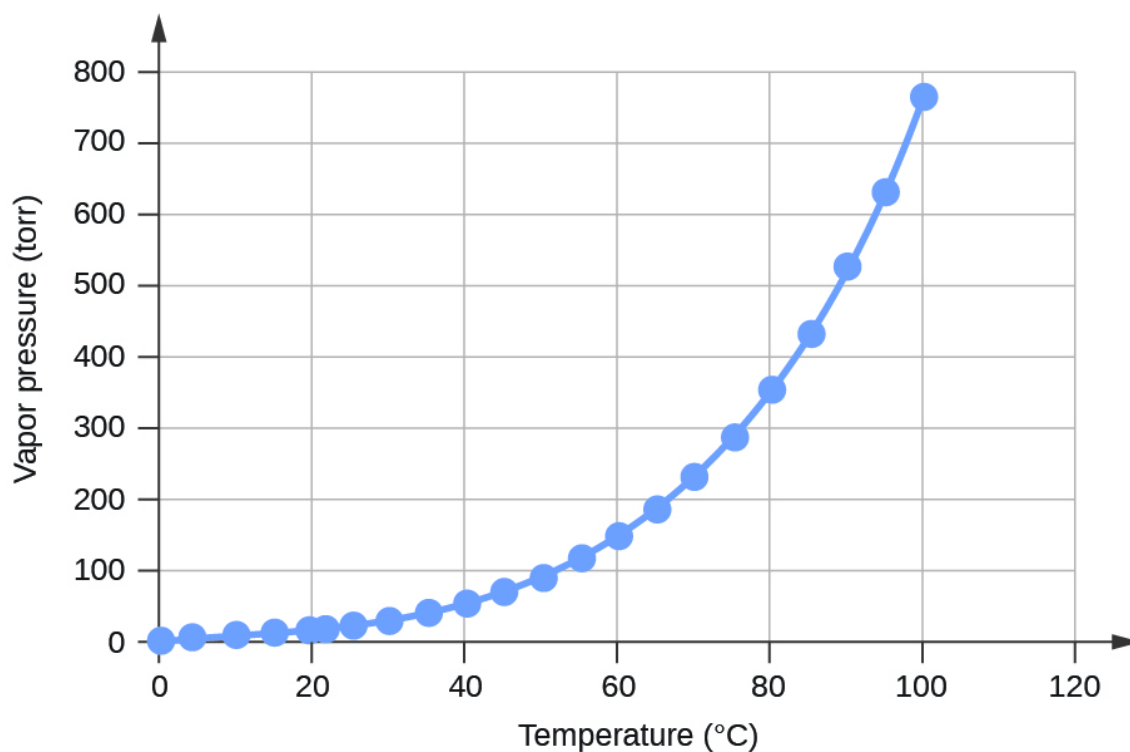


Water Vapor Pressure at Different Temperatures (°C)		
Temperature	Vapor Pressure (torr)	Vapor Pressure (Pa)
0	4.6	613.2812
4	6.1	813.2642
10	9.2	1226.562
15	12.8	1706.522

Water Vapor Pressure at Different Temperatures (°C)		
Temperature	Vapor Pressure (torr)	Vapor Pressure (Pa)
20	17.5	2333.135
22	19.8	2639.776
25	23.8	3173.064
30	31.8	4239.64
35	42.2	5626.188
40	55.3	7372.707
45	71.9	9585.852
50	92.5	12332.29
55	118.0	15732
60	149.4	19918.31
65	187.5	24997.88
70	233.7	31157.35
75	289.1	38543.39
80	355.1	47342.64
85	433.6	57808.42
90	525.8	70100.71

Water Vapor Pressure at Different Temperatures (°C)		
Temperature	Vapor Pressure (torr)	Vapor Pressure (Pa)
95	633.9	84512.82
100	760.0	101324.7

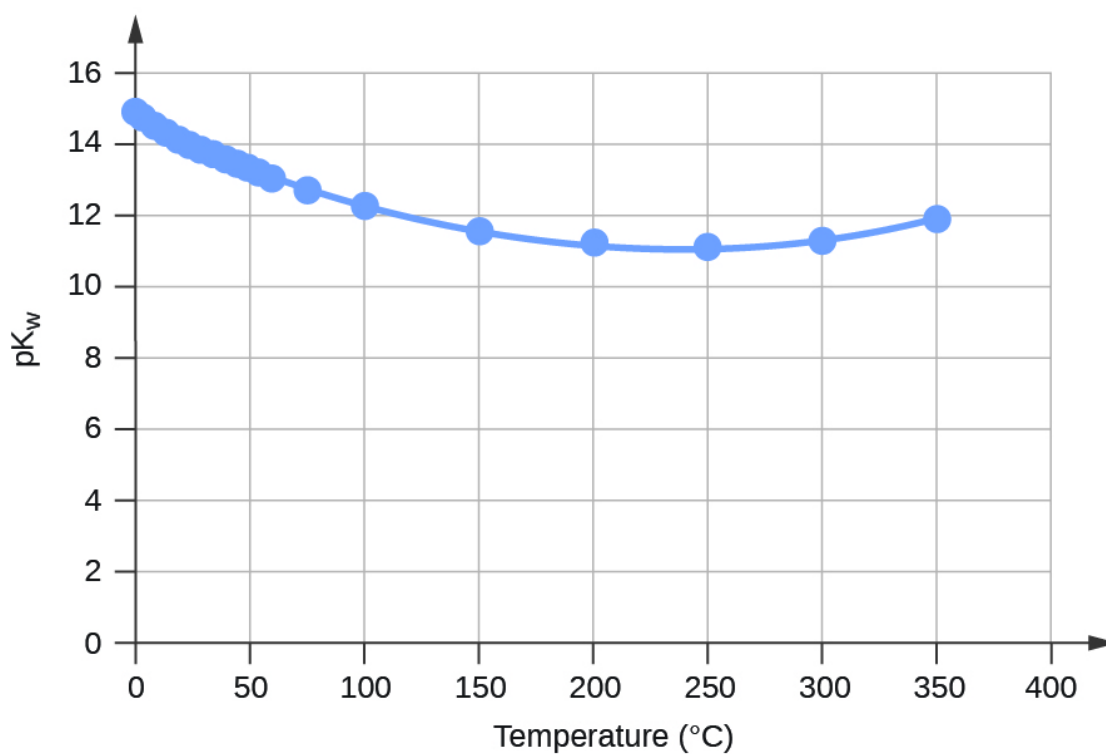
Vapor Pressure as a Function of Temperature



Water K_w and pK_w at Different Temperatures (°C)

Water K_w and pK_w at Different Temperatures (°C)		
Temperature	$K_w \cdot 10^{-14}$	$pK_w = -\log_{10}(K_w)$
Temperature	$K_w \cdot 10^{-14}$	pK_w $pK_w = -\log_{10}(K_w)$
0	0.112	14.95
5	0.182	14.74
10	0.288	14.54
15	0.465	14.33
20	0.671	14.17
25	0.991	14.00
30	1.432	13.84
35	2.042	13.69
40	2.851	13.55
45	3.917	13.41
50	5.297	13.28
55	7.080	13.15
60	9.311	13.03
75	19.95	12.70
100	56.23	12.25

Water pK_w as a Function of Temperature



Specific Heat Capacity for Water

$$C^\circ(\text{H}_2\text{O}(l)) = 4184 \text{ J}\cdot\text{K}^{-1}\cdot\text{kg}^{-1} = 4.184 \text{ J}\cdot\text{g}^{-1}\cdot^\circ\text{C}^{-1}$$

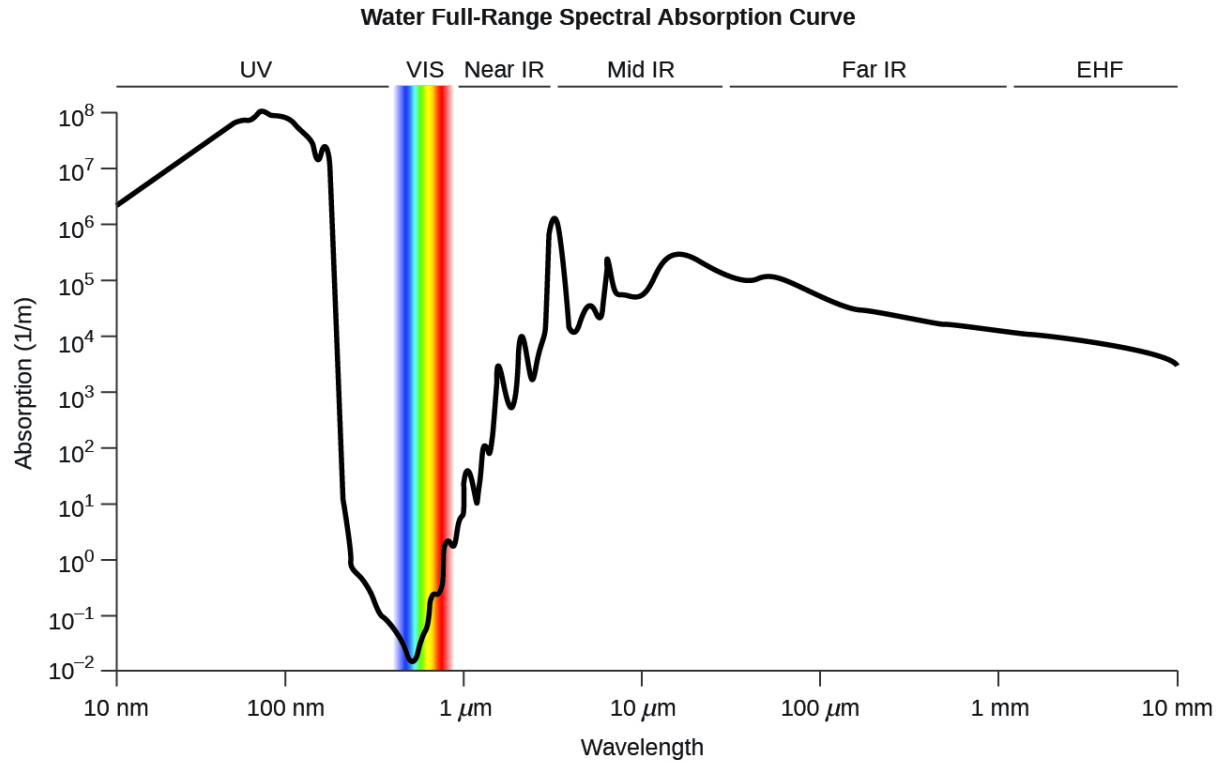
$$C^\circ(\text{H}_2\text{O}(s)) = 1864 \text{ J}\cdot\text{K}^{-1}\cdot\text{kg}^{-1}$$

$$C^\circ(\text{H}_2\text{O}(g)) = 2093 \text{ J}\cdot\text{K}^{-1}\cdot\text{kg}^{-1}$$

Standard Water Melting and Boiling Temperatures and Enthalpies of the Transitions		
	Temperature (K)	ΔH (kJ/mol)
melting	273.15	6.088
boiling	373.15	40.656 (44.016 at 298 K)

	Temperature (K)	ΔH (kJ/mol)
melting	273.15	6.088
boiling	373.15	40.656 (44.016 at 298 K)

Water Cryoscopic (Freezing Point Depression) and Ebullioscopic (Boiling Point Elevation) Constants
$K_f = 1.86^{\circ}\text{C}\cdot\text{kg}\cdot\text{mol}^{-1}$ (cryoscopic constant)
$K_b = 0.51^{\circ}\text{C}\cdot\text{kg}\cdot\text{mol}^{-1}$ (ebullioscopic constant)



Water full-range spectral absorption curve. This curve shows the full-range spectral absorption for water. The y-axis signifies the absorption in 1/cm. If we divide 1 by this value, we will obtain the length of the path (in cm) after which the intensity of a light beam passing through water decays by a factor of the base of the natural logarithm e ($e = 2.718281828$).

Composition of Commercial Acids and Bases

Composition of Commercial Acids and Bases			
Acid or Base[footnote] Acids and bases are commercially available as aqueous solutions. This table lists properties (densities and concentrations) of common acid and base solutions. Nominal values are provided in cases where the manufacturer cites a range of concentrations and densities.	Density (g/mL) [footnote] This column contains specific gravity data. In the case of this table, specific gravity is the ratio of density of a substance to the density of pure water at the same conditions. Specific gravity is often cited on commercial labels.	Percentage by Mass	Molarity
acetic acid, glacial	1.05	99.5%	17.4

aqueous ammonia [footnote] This solution is sometimes called “ammonium hydroxide,” although this term is not chemically accurate.	0.90	28%	14.8
hydrochloric acid	1.18	36%	11.6
nitric acid	1.42	71%	16.0
perchloric acid	1.67	70%	11.65
phosphoric acid	1.70	85%	14.7
sodium hydroxide	1.53	50%	19.1
sulfuric acid	1.84	96%	18.0

Standard Thermodynamic Properties for Selected Substances

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
aluminum			
Al(s)	0	0	28.3
Al(g)	324.4	285.7	164.54
Al ³⁺ (aq)	-531	-485	-321.7
Al ₂ O ₃ (s)	-1676	-1582	50.92
AlF ₃ (s)	-1510.4	-1425	66.5
AlCl ₃ (s)	-704.2	-628.8	110.67
AlCl ₃ ·6H ₂ O(s)	-2691.57	-2269.40	376.56
Al ₂ S ₃ (s)	-724.0	-492.4	116.9
Al ₂ (SO ₄) ₃ (s)	-3445.06	-3506.61	239.32
antimony			

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
Sb(s)	0	0	45.69
Sb(g)	262.34	222.17	180.16
Sb ₄ O ₆ (s)	— 1440.55	−1268.17	220.92
SbCl ₃ (g)	−313.8	−301.2	337.80
SbCl ₅ (g)	−394.34	−334.29	401.94
Sb ₂ S ₃ (s)	−174.89	−173.64	182.00
SbCl ₃ (s)	−382.17	−323.72	184.10
SbOCl(s)	−374.0	—	—
arsenic			
As(s)	0	0	35.1
As(g)	302.5	261.0	174.21
As ₄ (g)	143.9	92.4	314
As ₄ O ₆ (s)	— 1313.94	−1152.52	214.22
As ₂ O ₅ (s)	−924.87	−782.41	105.44

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
AsCl ₃ (g)	-261.50	-248.95	327.06
As ₂ S ₃ (s)	-169.03	-168.62	163.59
AsH ₃ (g)	66.44	68.93	222.78
H ₃ AsO ₄ (s)	-906.3	—	—
barium			
Ba(s)	0	0	62.5
Ba(g)	180	146	170.24
Ba ²⁺ (aq)	-537.6	-560.8	9.6
BaO(s)	-548.0	-520.3	72.1
BaCl ₂ (s)	-855.0	-806.7	123.7
BaSO ₄ (s)	-1473.2	-1362.3	132.2
beryllium			
Be(s)	0	0	9.50
Be(g)	324.3	286.6	136.27
BeO(s)	-609.4	-580.1	13.8

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
bismuth			
Bi(s)	0	0	56.74
Bi(g)	207.1	168.2	187.00
Bi ₂ O ₃ (s)	-573.88	-493.7	151.5
BiCl ₃ (s)	-379.07	-315.06	176.98
Bi ₂ S ₃ (s)	-143.1	-140.6	200.4
boron			
B(s)	0	0	5.86
B(g)	565.0	521.0	153.4
B ₂ O ₃ (s)	-1273.5	-1194.3	53.97
B ₂ H ₆ (g)	36.4	87.6	232.1
H ₃ BO ₃ (s)	-1094.33	-968.92	88.83
BF ₃ (g)	-1136.0	-1119.4	254.4
BCl ₃ (g)	-403.8	-388.7	290.1
B ₃ N ₃ H ₆ (l)	-540.99	-392.79	199.58

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
HBO ₂ (s)	-794.25	-723.41	37.66
bromine			
Br ₂ (l)	0	0	152.23
Br ₂ (g)	30.91	3.142	245.5
Br(g)	111.88	82.429	175.0
Br ⁻ (aq)	-120.9	-102.82	80.71
BrF ₃ (g)	-255.60	-229.45	292.42
HBr(g)	-36.3	-53.43	198.7
cadmium			
Cd(s)	0	0	51.76
Cd(g)	112.01	77.41	167.75
Cd ²⁺ (aq)	-75.90	-77.61	-73.2
CdO(s)	-258.2	-228.4	54.8
CdCl ₂ (s)	-391.5	-343.9	115.3
CdSO ₄ (s)	-933.3	-822.7	123.0

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
CdS(s)	-161.9	-156.5	64.9
calcium			
Ca(s)	0	0	41.6
Ca(g)	178.2	144.3	154.88
Ca ²⁺ (aq)	-542.96	-553.04	-55.2
CaO(s)	-634.9	-603.3	38.1
Ca(OH) ₂ (s)	-985.2	-897.5	83.4
CaSO ₄ (s)	-1434.5	-1322.0	106.5
CaSO ₄ ·2H ₂ O(s)	-2022.63	-1797.45	194.14
CaCO ₃ (s) (calcite)	-1220.0	-1081.4	110.0
CaSO ₃ ·H ₂ O(s)	-1752.68	-1555.19	184.10
carbon			
C(s) (graphite)	0	0	5.740
C(s) (diamond)	1.89	2.90	2.38

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
C(<i>g</i>)	716.681	671.2	158.1
CO(<i>g</i>)	-110.52	-137.15	197.7
CO ₂ (<i>g</i>)	-393.51	-394.36	213.8
CO ₃ ²⁻ (<i>aq</i>)	-677.1	-527.8	-56.9
CH ₄ (<i>g</i>)	-74.6	-50.5	186.3
CH ₃ OH(<i>l</i>)	-239.2	-166.6	126.8
CH ₃ OH(<i>g</i>)	-201.0	-162.3	239.9
CCl ₄ (<i>l</i>)	-128.2	-62.5	214.4
CCl ₄ (<i>g</i>)	-95.7	-58.2	309.7
CHCl ₃ (<i>l</i>)	-134.1	-73.7	201.7
CHCl ₃ (<i>g</i>)	-103.14	-70.34	295.71
CS ₂ (<i>l</i>)	89.70	65.27	151.34
CS ₂ (<i>g</i>)	116.9	66.8	238.0
C ₂ H ₂ (<i>g</i>)	227.4	209.2	200.9
C ₂ H ₄ (<i>g</i>)	52.4	68.4	219.3

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
C ₂ H ₆ (g)	-84.0	-32.0	229.2
CH ₃ CO ₂ H(l)	-484.3	-389.9	159.8
CH ₃ CO ₂ H(g)	-434.84	-376.69	282.50
C ₂ H ₅ OH(l)	-277.6	-174.8	160.7
C ₂ H ₅ OH(g)	-234.8	-167.9	281.6
HCO ₃ ⁻ (aq)	-691.11	-587.06	95
C ₃ H ₈ (g)	-103.8	-23.4	270.3
C ₆ H ₆ (g)	82.927	129.66	269.2
C ₆ H ₆ (l)	49.1	124.50	173.4
CH ₂ Cl ₂ (l)	-124.2	-63.2	177.8
CH ₂ Cl ₂ (g)	-95.4	-65.90	270.2
CH ₃ Cl(g)	-81.9	-60.2	234.6
C ₂ H ₅ Cl(l)	-136.52	-59.31	190.79
C ₂ H ₅ Cl(g)	-112.17	-60.39	276.00
C ₂ N ₂ (g)	308.98	297.36	241.90

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
HCN(<i>l</i>)	108.9	125.0	112.8
HCN(<i>g</i>)	135.5	124.7	201.8
cesium			
Cs ⁺ (<i>aq</i>)	−248	−282.0	133
chlorine			
Cl ₂ (<i>g</i>)	0	0	223.1
Cl(<i>g</i>)	121.3	105.70	165.2
Cl [−] (<i>aq</i>)	−167.2	−131.2	56.5
ClF(<i>g</i>)	−54.48	−55.94	217.78
ClF ₃ (<i>g</i>)	−158.99	−118.83	281.50
Cl ₂ O(<i>g</i>)	80.3	97.9	266.2
Cl ₂ O ₇ (<i>l</i>)	238.1	—	—
Cl ₂ O ₇ (<i>g</i>)	272.0	—	—
HCl(<i>g</i>)	−92.307	−95.299	186.9
HClO ₄ (<i>l</i>)	−40.58	—	—

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
chromium			
Cr(s)	0	0	23.77
Cr(g)	396.6	351.8	174.50
CrO ₄ ²⁻ (aq)	-881.2	-727.8	50.21
Cr ₂ O ₇ ²⁻ (aq)	-1490.3	-1301.1	261.9
Cr ₂ O ₃ (s)	-1139.7	-1058.1	81.2
CrO ₃ (s)	-589.5	—	—
(NH ₄) ₂ Cr ₂ O ₇ (s)	-1806.7	—	—
cobalt			
Co(s)	0	0	30.0
Co ²⁺ (aq)	-67.4	-51.5	-155
Co ³⁺ (aq)	92	134	-305.0
CoO(s)	-237.9	-214.2	52.97
Co ₃ O ₄ (s)	-910.02	-794.98	114.22
Co(NO ₃) ₂ (s)	-420.5	—	—

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
copper			
Cu(s)	0	0	33.15
Cu(g)	338.32	298.58	166.38
Cu ⁺ (aq)	51.9	50.2	-26
Cu ²⁺ (aq)	64.77	65.49	-99.6
CuO(s)	-157.3	-129.7	42.63
Cu ₂ O(s)	-168.6	-146.0	93.14
CuS(s)	-53.1	-53.6	66.5
Cu ₂ S(s)	-79.5	-86.2	120.9
CuSO ₄ (s)	-771.36	-662.2	109.2
Cu(NO ₃) ₂ (s)	-302.9	—	—
fluorine			
F ₂ (g)	0	0	202.8
F(g)	79.4	62.3	158.8
F ⁻ (aq)	-332.6	-278.8	-13.8

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
F ₂ O(<i>g</i>)	24.7	41.9	247.43
HF(<i>g</i>)	-273.3	-275.4	173.8
hydrogen			
H ₂ (<i>g</i>)	0	0	130.7
H(<i>g</i>)	217.97	203.26	114.7
H ⁺ (<i>aq</i>)	0	0	0
OH ⁻ (<i>aq</i>)	-230.0	-157.2	-10.75
H ₃ O ⁺ (<i>aq</i>)	-285.8		69.91
H ₂ O(<i>l</i>)	-285.83	-237.1	70.0
H ₂ O(<i>g</i>)	-241.82	-228.59	188.8
H ₂ O ₂ (<i>l</i>)	-187.78	-120.35	109.6
H ₂ O ₂ (<i>g</i>)	-136.3	-105.6	232.7
HF(<i>g</i>)	-273.3	-275.4	173.8
HCl(<i>g</i>)	-92.307	-95.299	186.9
HBr(<i>g</i>)	-36.3	-53.43	198.7

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
HI(<i>g</i>)	26.48	1.70	206.59
H ₂ S(<i>g</i>)	−20.6	−33.4	205.8
H ₂ Se(<i>g</i>)	29.7	15.9	219.0
iodine			
I ₂ (<i>s</i>)	0	0	116.14
I ₂ (<i>g</i>)	62.438	19.3	260.7
I(<i>g</i>)	106.84	70.2	180.8
I [−] (<i>aq</i>)	−55.19	−51.57	11.13
IF(<i>g</i>)	95.65	−118.49	236.06
ICl(<i>g</i>)	17.78	−5.44	247.44
IBr(<i>g</i>)	40.84	3.72	258.66
IF ₇ (<i>g</i>)	−943.91	−818.39	346.44
HI(<i>g</i>)	26.48	1.70	206.59
iron			
Fe(<i>s</i>)	0	0	27.3

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
Fe(<i>g</i>)	416.3	370.7	180.5
Fe ²⁺ (<i>aq</i>)	-89.1	-78.90	-137.7
Fe ³⁺ (<i>aq</i>)	-48.5	-4.7	-315.9
Fe ₂ O ₃ (<i>s</i>)	-824.2	-742.2	87.40
Fe ₃ O ₄ (<i>s</i>)	-1118.4	-1015.4	146.4
Fe(CO) ₅ (<i>l</i>)	-774.04	-705.42	338.07
Fe(CO) ₅ (<i>g</i>)	-733.87	-697.26	445.18
FeCl ₂ (<i>s</i>)	-341.79	-302.30	117.95
FeCl ₃ (<i>s</i>)	-399.49	-334.00	142.3
FeO(<i>s</i>)	-272.0	-255.2	60.75
Fe(OH) ₂ (<i>s</i>)	-569.0	-486.5	88.
Fe(OH) ₃ (<i>s</i>)	-823.0	-696.5	106.7
FeS(<i>s</i>)	-100.0	-100.4	60.29
Fe ₃ C(<i>s</i>)	25.10	20.08	104.60
lead			

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
Pb(s)	0	0	64.81
Pb(g)	195.2	162.	175.4
Pb ²⁺ (aq)	-1.7	-24.43	10.5
PbO(s) (yellow)	-217.32	-187.89	68.70
PbO(s) (red)	-218.99	-188.93	66.5
Pb(OH) ₂ (s)	-515.9	—	—
PbS(s)	-100.4	-98.7	91.2
Pb(NO ₃) ₂ (s)	-451.9	—	—
PbO ₂ (s)	-277.4	-217.3	68.6
PbCl ₂ (s)	-359.4	-314.1	136.0
lithium			
Li(s)	0	0	29.1
Li(g)	159.3	126.6	138.8
Li ⁺ (aq)	-278.5	-293.3	13.4
LiH(s)	-90.5	-68.3	20.0

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
Li(OH)(s)	-487.5	-441.5	42.8
LiF(s)	-616.0	-587.5	35.7
Li ₂ CO ₃ (s)	-1216.04	-1132.19	90.17
magnesium			
Mg ²⁺ (aq)	-466.9	-454.8	-138.1
manganese			
Mn(s)	0	0	32.0
Mn(g)	280.7	238.5	173.7
Mn ²⁺ (aq)	-220.8	-228.1	-73.6
MnO(s)	-385.2	-362.9	59.71
MnO ₂ (s)	-520.03	-465.1	53.05
Mn ₂ O ₃ (s)	-958.97	-881.15	110.46
Mn ₃ O ₄ (s)	-1378.83	-1283.23	155.64
MnO ₄ ⁻ (aq)	-541.4	-447.2	191.2

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
MnO ₄ ²⁻ (aq)	−653.0	−500.7	59
mercury			
Hg(l)	0	0	75.9
Hg(g)	61.4	31.8	175.0
Hg ²⁺ (aq)		164.8	
Hg ²⁺ (aq)	172.4	153.9	84.5
HgO(s) (red)	−90.83	−58.5	70.29
HgO(s) (yellow)	−90.46	−58.43	71.13
HgCl ₂ (s)	−224.3	−178.6	146.0
Hg ₂ Cl ₂ (s)	−265.4	−210.7	191.6
HgS(s) (red)	−58.16	−50.6	82.4
HgS(s) (black)	−53.56	−47.70	88.28
HgSO ₄ (s)	−707.51	−594.13	0.00
nickel			
Ni ²⁺ (aq)	−64.0	−46.4	−159

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
nitrogen			
N ₂ (g)	0	0	191.6
N(g)	472.704	455.5	153.3
NO(g)	90.25	87.6	210.8
NO ₂ (g)	33.2	51.30	240.1
N ₂ O(g)	81.6	103.7	220.0
N ₂ O ₃ (g)	83.72	139.41	312.17
NO ₃ ⁻ (aq)	-205.0	-108.7	146.4
N ₂ O ₄ (g)	11.1	99.8	304.4
N ₂ O ₅ (g)	11.3	115.1	355.7
NH ₃ (g)	-45.9	-16.5	192.8
NH ₄ ⁺ (aq)	-132.5	-79.31	113.4
N ₂ H ₄ (l)	50.63	149.43	121.21
N ₂ H ₄ (g)	95.4	159.4	238.5
NH ₄ NO ₃ (s)	-365.56	-183.87	151.08

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
NH ₄ Cl(s)	-314.43	-202.87	94.6
NH ₄ Br(s)	-270.8	-175.2	113.0
NH ₄ I(s)	-201.4	-112.5	117.0
NH ₄ NO ₂ (s)	-256.5	—	—
HNO ₃ (l)	-174.1	-80.7	155.6
HNO ₃ (g)	-133.9	-73.5	266.9
oxygen			
O ₂ (g)	0	0	205.2
O(g)	249.17	231.7	161.1
O ₃ (g)	142.7	163.2	238.9
phosphorus			
P ₄ (s)	0	0	164.4
P ₄ (g)	58.91	24.4	280.0
P(g)	314.64	278.25	163.19
PH ₃ (g)	5.4	13.5	210.2

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
PCl ₃ (g)	-287.0	-267.8	311.78
PCl ₅ (g)	-374.9	-305.0	364.4
P ₄ O ₆ (s)	-1640.1	—	—
P ₄ O ₁₀ (s)	-2984.0	-2697.0	228.86
PO ₄ ³⁻ (aq)	-1277	-1019	-222
HPO ₃ (s)	-948.5	—	—
HPO ₄ ²⁻ (aq)	-1292.1	-1089.3	-33
H ₂ PO ₄ ²⁻ (aq)	-1296.3	-1130.4	90.4
H ₃ PO ₂ (s)	-604.6	—	—
H ₃ PO ₃ (s)	-964.4	—	—
H ₃ PO ₄ (s)	-1279.0	-1119.1	110.50
H ₃ PO ₄ (l)	-1266.9	-1124.3	110.5
H ₄ P ₂ O ₇ (s)	-2241.0	—	—
POCl ₃ (l)	-597.1	-520.8	222.5
POCl ₃ (g)	-558.5	-512.9	325.5

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
potassium			
K(s)	0	0	64.7
K(g)	89.0	60.5	160.3
K ⁺ (aq)	-252.4	-283.3	102.5
KF(s)	-576.27	-537.75	66.57
KCl(s)	-436.5	-408.5	82.6
rubidium			
Rb ⁺ (aq)	-246	-282.2	124
silicon			
Si(s)	0	0	18.8
Si(g)	450.0	405.5	168.0
SiO ₂ (s)	-910.7	-856.3	41.5
SiH ₄ (g)	34.3	56.9	204.6
H ₂ SiO ₃ (s)	-1188.67	-1092.44	133.89

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
H ₄ SiO ₄ (s)	-1481.14	-1333.02	192.46
SiF ₄ (g)	-1615.0	-1572.8	282.8
SiCl ₄ (l)	-687.0	-619.8	239.7
SiCl ₄ (g)	-662.75	-622.58	330.62
SiC(s, <i>beta cubic</i>)	-73.22	-70.71	16.61
SiC(s, <i>alpha hexagonal</i>)	-71.55	-69.04	16.48
silver			
Ag(s)	0	0	42.55
Ag(g)	284.9	246.0	172.89
Ag ⁺ (aq)	105.6	77.11	72.68
Ag ₂ O(s)	-31.05	-11.20	121.3
AgCl(s)	-127.0	-109.8	96.3
Ag ₂ S(s)	-32.6	-40.7	144.0
sodium			

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
Na(s)	0	0	51.3
Na(g)	107.5	77.0	153.7
Na ⁺ (aq)	-240.1	-261.9	59
Na ₂ O(s)	-414.2	-375.5	75.1
NaCl(s)	-411.2	-384.1	72.1
strontium			
Sr ²⁺ (aq)	-545.8	-557.3	-32.6
sulfur			
S ₈ (s) (rhombic)	0	0	256.8
S(g)	278.81	238.25	167.82
S ²⁻ (aq)	41.8	83.7	22
SO ₂ (g)	-296.83	-300.1	248.2
SO ₃ (g)	-395.72	-371.06	256.76
SO ₄ ²⁻ (aq)	-909.3	-744.5	20.1
S ₂ O ₃ ²⁻ (aq)	-648.5	-522.5	67

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
H ₂ S(g)	-20.6	-33.4	205.8
HS ⁻ (aq)	-17.7	12.6	61.1
H ₂ SO ₄ (l)	-813.989	690.00	156.90
HSO ₄ ²⁻ (aq)	-885.75	-752.87	126.9
H ₂ S ₂ O ₇ (s)	-1273.6	—	—
SF ₄ (g)	-728.43	-684.84	291.12
SF ₆ (g)	-1220.5	-1116.5	291.5
SCl ₂ (l)	-50	—	—
SCl ₂ (g)	-19.7	—	—
S ₂ Cl ₂ (l)	-59.4	—	—
S ₂ Cl ₂ (g)	-19.50	-29.25	319.45
SOCl ₂ (g)	-212.55	-198.32	309.66
SOCl ₂ (l)	-245.6	—	—
SO ₂ Cl ₂ (l)	-394.1	—	—
SO ₂ Cl ₂ (g)	-354.80	-310.45	311.83

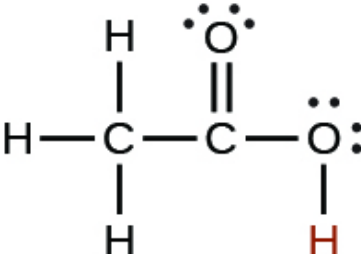
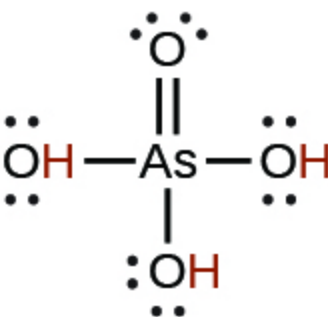
Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
tin			
Sn(s)	0	0	51.2
Sn(g)	301.2	266.2	168.5
SnO(s)	-285.8	-256.9	56.5
SnO ₂ (s)	-577.6	-515.8	49.0
SnCl ₄ (l)	-511.3	-440.1	258.6
SnCl ₄ (g)	-471.5	-432.2	365.8
titanium			
Ti(s)	0	0	30.7
Ti(g)	473.0	428.4	180.3
TiO ₂ (s)	-944.0	-888.8	50.6
TiCl ₄ (l)	-804.2	-737.2	252.4
TiCl ₄ (g)	-763.2	-726.3	353.2
tungsten			
W(s)	0	0	32.6

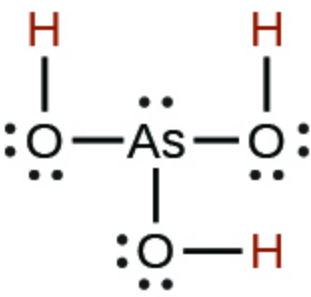
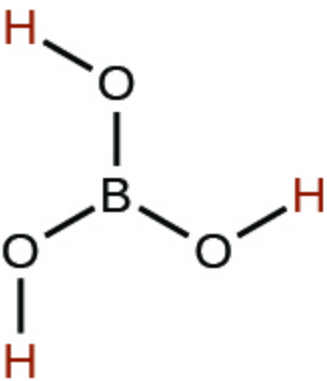
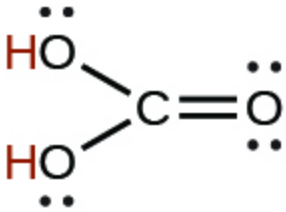
Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
W(g)	849.4	807.1	174.0
WO ₃ (s)	-842.9	-764.0	75.9
zinc			
Zn(s)	0	0	41.6
Zn(g)	130.73	95.14	160.98
Zn ²⁺ (aq)	-153.9	-147.1	-112.1
ZnO(s)	-350.5	-320.5	43.7
ZnCl ₂ (s)	-415.1	-369.43	111.5
ZnS(s)	-206.0	-201.3	57.7
ZnSO ₄ (s)	-982.8	-871.5	110.5
ZnCO ₃ (s)	-812.78	-731.57	82.42
complexes			
[Co(NH ₃) ₄ (NO ₂) ₂]NO ₃ , <i>cis</i>	-898.7	—	—
[Co(NH ₃) ₄ (NO ₂) ₂]NO ₃ , <i>trans</i>	-896.2	—	—

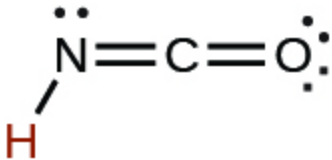
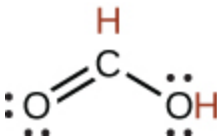
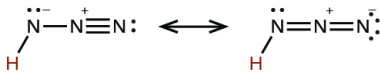
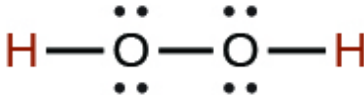
Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
NH ₄ [Co(NH ₃) ₂ (NO ₂) ₄]	−837.6	—	—
[Co(NH ₃) ₆] [Co(NH ₃) ₂ (NO ₂) ₄] ₃	−2733.0	—	—
[Co(NH ₃) ₄ Cl ₂]Cl, <i>cis</i>	−874.9	—	—
[Co(NH ₃) ₄ Cl ₂]Cl, <i>trans</i>	−877.4	—	—
[Co(en) ₂ (NO ₂) ₂]NO ₃ , <i>cis</i>	−689.5	—	—
[Co(en) ₂ Cl ₂]Cl, <i>cis</i>	−681.2	—	—
[Co(en) ₂ Cl ₂]Cl, <i>trans</i>	−677.4	—	—
[Co(en) ₃](ClO ₄) ₃	−762.7	—	—
[Co(en) ₃]Br ₂	−595.8	—	—
[Co(en) ₃]I ₂	−475.3	—	—
[Co(en) ₃]I ₃	−519.2	—	—
[Co(NH ₃) ₆](ClO ₄) ₃	−1034.7	−221.1	615
[Co(NH ₃) ₅ NO ₂](NO ₃) ₂	−1088.7	−412.9	331
[Co(NH ₃) ₆](NO ₃) ₃	−1282.0	−524.5	448

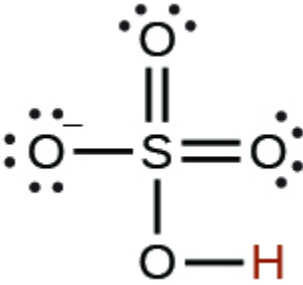
Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)
[Co(NH ₃) ₅ Cl]Cl ₂	-1017.1	-582.5	366.1
[Pt(NH ₃) ₄]Cl ₂	-725.5	—	—
[Ni(NH ₃) ₆]Cl ₂	-994.1	—	—
[Ni(NH ₃) ₆]Br ₂	-923.8	—	—
[Ni(NH ₃) ₆]I ₂	-808.3	—	—

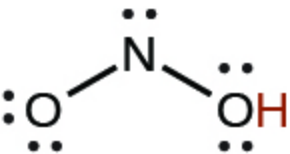
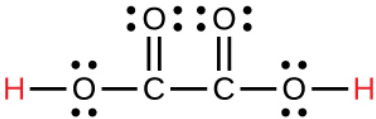
Ionization Constants of Weak Acids

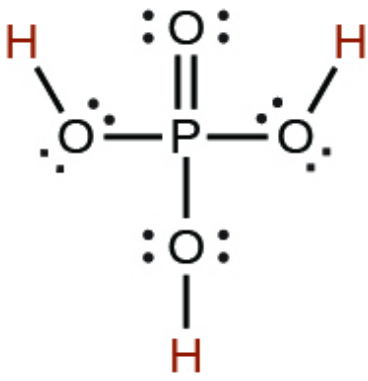
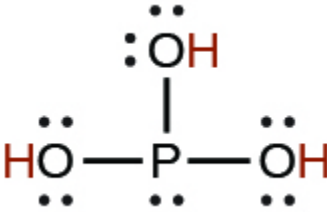
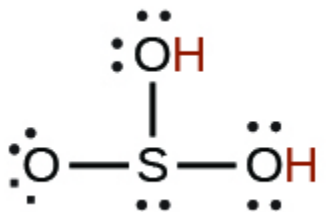
Ionization Constants of Weak Acids			
Acid	Formula	K_a at 25 °C	Lewis Structure
acetic	$\text{CH}_3\text{CO}_2\text{H}$	1.8×10^{-5}	
arsenic	H_3AsO_4	5.5×10^{-3}	
	H_2AsO_4^-	1.7×10^{-7}	
	HAsO_4^{2-}	5.1×10^{-12}	

Ionization Constants of Weak Acids			
Acid	Formula	K_a at 25 °C	Lewis Structure
arsenous	H_3AsO_3	5.1×10^{-10}	
boric	H_3BO_3	5.4×10^{-10}	
carbonic	H_2CO_3	4.3×10^{-7}	
	HCO_3^-	4.7×10^{-11}	

Ionization Constants of Weak Acids			
Acid	Formula	K_a at 25 °C	Lewis Structure
cyanic	HCNO	2×10^{-4}	
formic	HCO ₂ H	1.8×10^{-4}	
hydrazoic	HN ₃	2.5×10^{-5}	
hydrocyanic	HCN	4.9×10^{-10}	
hydrofluoric	HF	3.5×10^{-4}	
hydrogen peroxide	H ₂ O ₂	2.4×10^{-12}	

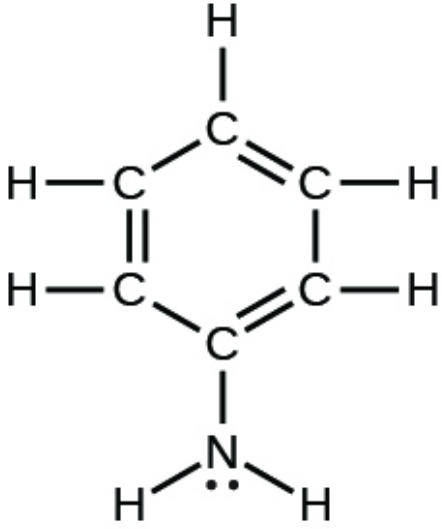
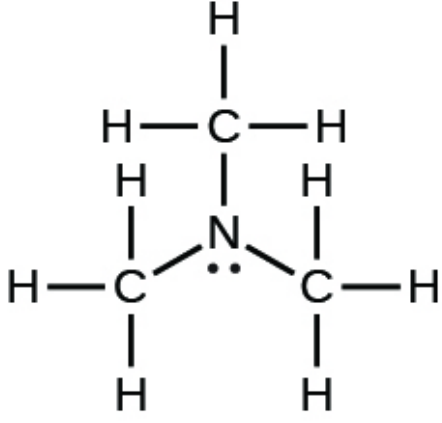
Ionization Constants of Weak Acids			
Acid	Formula	K_a at 25 °C	Lewis Structure
hydrogen selenide	H_2Se	1.29×10^{-4}	
	HSe^-	1×10^{-12}	
hydrogen sulfate ion	HSO_4^-	1.2×10^{-2}	
hydrogen sulfide	H_2S	8.9×10^{-8}	
	HS^-	1.0×10^{-19}	
hydrogen telluride	H_2Te	2.3×10^{-3}	

Ionization Constants of Weak Acids			
Acid	Formula	K_a at 25 °C	Lewis Structure
	HTe^-	1.6×10^{-11}	
hypobromous	HBrO	2.8×10^{-9}	
hypochlorous	HClO	2.9×10^{-8}	
nitrous	HNO_2	4.6×10^{-4}	
oxalic	$\text{H}_2\text{C}_2\text{O}_4$	6.0×10^{-2}	
	HC_2O_4^-	6.1×10^{-5}	
phosphoric	H_3PO_4	7.5×10^{-3}	

Ionization Constants of Weak Acids			
Acid	Formula	K_a at 25 °C	Lewis Structure
	H_2PO_4^-	6.2×10^{-8}	
	HPO_4^{2-}	4.2×10^{-13}	
phosphorous	H_3PO_3	5×10^{-2}	
	H_2PO_3^-	2.0×10^{-7}	
sulfurous	H_2SO_3	1.6×10^{-2}	
	HSO_3^-	6.4×10^{-8}	

Ionization Constants of Weak Bases

Ionization Constants of Weak Bases		
Base	Lewis Structure	K_b at 25 °C
ammonia	$\begin{array}{c} \text{H} - \ddot{\text{N}} - \text{H} \\ \\ \text{H} \end{array}$	1.8×10^{-5}
dimethylamine	$\begin{array}{ccccc} & \text{H} & & \text{H} & \\ & & & & \\ \text{H} & - \text{C} & - & \text{N} & - \text{C} - \text{H} \\ & & & \ddot{} & \\ & \text{H} & & & \text{H} \end{array}$	5.9×10^{-4}
methylamine	$\begin{array}{ccccc} & \text{H} & & & \\ & & & & \\ \text{H} & - \text{C} & - & \ddot{\text{N}} & - \text{H} \\ & & & & \\ & \text{H} & & \text{H} & \end{array}$	4.4×10^{-4}

Ionization Constants of Weak Bases		
Base	Lewis Structure	K_b at 25 °C
phenylamine (aniline)		4.3×10^{-10}
trimethylamine		6.3×10^{-5}

Formation Constants for Complex Ions

Formation Constants for Complex Ions	
Equilibrium	K_f
$\text{Al}^{3+} + 6\text{F}^- \rightleftharpoons [\text{AlF}_6]^{3-}$	7×10^{19}
$\text{Cd}^{2+} + 4\text{NH}_3 \rightleftharpoons [\text{Cd}(\text{NH}_3)_4]^{2+}$	1.3×10^7
$\text{Cd}^{2+} + 4\text{CN}^- \rightleftharpoons [\text{Cd}(\text{CN})_4]^{2-}$	3×10^{18}
$\text{Co}^{2+} + 6\text{NH}_3 \rightleftharpoons [\text{Co}(\text{NH}_3)_6]^{2+}$	1.3×10^5
$\text{Co}^{3+} + 6\text{NH}_3 \rightleftharpoons [\text{Co}(\text{NH}_3)_6]^{3+}$	2.3×10^{33}
$\text{Cu}^+ + 2\text{CN}^- \rightleftharpoons [\text{Cu}(\text{CN})_2]^-$	1.0×10^{16}
$\text{Cu}^{2+} + 4\text{NH}_3 \rightleftharpoons [\text{Cu}(\text{NH}_3)_4]^{2+}$	1.7×10^{13}
$\text{Fe}^{2+} + 6\text{CN}^- \rightleftharpoons [\text{Fe}(\text{CN})_6]^{4-}$	1.5×10^{35}
$\text{Fe}^{3+} + 6\text{CN}^- \rightleftharpoons [\text{Fe}(\text{CN})_6]^{3-}$	2×10^{43}
$\text{Fe}^{3+} + 6\text{SCN}^- \rightleftharpoons [\text{Fe}(\text{SCN})_6]^{3-}$	3.2×10^3
$\text{Hg}^{2+} + 4\text{Cl}^- \rightleftharpoons [\text{HgCl}_4]^{2-}$	1.1×10^{16}
$\text{Ni}^{2+} + 6\text{NH}_3 \rightleftharpoons [\text{Ni}(\text{NH}_3)_6]^{2+}$	2.0×10^8

Formation Constants for Complex Ions	
Equilibrium	K_f
$\text{Ag}^+ + 2\text{Cl}^- \rightleftharpoons [\text{AgCl}_2]^-$	1.8×10^5
$\text{Ag}^+ + 2\text{CN}^- \rightleftharpoons [\text{Ag}(\text{CN})_2]^-$	1×10^{21}
$\text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+$	1.7×10^7
$\text{Zn}^{2+} + 4\text{CN}^- \rightleftharpoons [\text{Zn}(\text{CN})_4]^{2-}$	2.1×10^{19}
$\text{Zn}^{2+} + 4\text{OH}^- \rightleftharpoons [\text{Zn}(\text{OH})_4]^{2-}$	2×10^{15}
$\text{Fe}^{3+} + \text{SCN}^- \rightleftharpoons [\text{Fe}(\text{SCN})]^{2+}$	8.9×10^2
$\text{Ag}^+ + 4\text{SCN}^- \rightleftharpoons [\text{Ag}(\text{SCN})_4]^{3-}$	1.2×10^{10}
$\text{Pb}^{2+} + 4\text{I}^- \rightleftharpoons [\text{PbI}_4]^{2-}$	3.0×10^4
$\text{Pt}^{2+} + 4\text{Cl}^- \rightleftharpoons [\text{PtCl}_4]^{2-}$	1×10^{16}
$\text{Cu}^{2+} + 4\text{CN}^- \rightleftharpoons [\text{Cu}(\text{CN})_4]^{2-}$	1.0×10^{25}
$\text{Co}^{2+} + 4\text{SCN}^- \rightleftharpoons [\text{Co}(\text{SCN})_4]^{2-}$	1×10^3

Standard Electrode (Half-Cell) Potentials

Standard Electrode (Half-Cell) Potentials	
Half-Reaction	E° (V)
$\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag}$	+0.7996
$\text{AgCl} + \text{e}^- \longrightarrow \text{Ag} + \text{Cl}^-$	+0.22233
$[\text{Ag}(\text{CN})_2]^- + \text{e}^- \longrightarrow \text{Ag} + 2\text{CN}^-$	-0.31
$\text{Ag}_2\text{CrO}_4 + 2\text{e}^- \longrightarrow 2\text{Ag} + \text{CrO}_4^{2-}$	+0.45
$[\text{Ag}(\text{NH}_3)_2]^+ + \text{e}^- \longrightarrow \text{Ag} + 2\text{NH}_3$	+0.373
$[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3+} + \text{e}^- \longrightarrow \text{Ag} + 2\text{S}_2\text{O}_3^{2-}$	+0.017
$[\text{AlF}_6]^{3-} + 3\text{e}^- \longrightarrow \text{Al} + 6\text{F}^-$	-2.07
$\text{Al}^{3+} + 3\text{e}^- \longrightarrow \text{Al}$	-1.662
$\text{Am}^{3+} + 3\text{e}^- \longrightarrow \text{Am}$	-2.048
$\text{Au}^{3+} + 3\text{e}^- \longrightarrow \text{Au}$	+1.498
$\text{Au}^+ + \text{e}^- \longrightarrow \text{Au}$	+1.692
$\text{Ba}^{2+} + 2\text{e}^- \longrightarrow \text{Ba}$	-2.912
$\text{Be}^{2+} + 2\text{e}^- \longrightarrow \text{Be}$	-1.847

Standard Electrode (Half-Cell) Potentials	
Half-Reaction	E° (V)
$\text{Br}_2(aq) + 2e^- \longrightarrow 2\text{Br}^-$	+1.0873
$\text{Ca}^{2+} + 2e^- \longrightarrow \text{Ca}$	-2.868
$\text{Ce}^3 + 3e^- \longrightarrow \text{Ce}$	-2.483
$\text{Ce}^{4+} + e^- \longrightarrow \text{Ce}^{3+}$	+1.61
$\text{Cd}^{2+} + 2e^- \longrightarrow \text{Cd}$	-0.4030
$[\text{Cd}(\text{CN})_4]^{2-} + 2e^- \longrightarrow \text{Cd} + 4\text{CN}^-$	-1.09
$[\text{Cd}(\text{NH}_3)_4]^{2+} + 2e^- \longrightarrow \text{Cd} + 4\text{NH}_3$	-0.61
$\text{CdS} + 2e^- \longrightarrow \text{Cd} + \text{S}^{2-}$	-1.17
$\text{Cl}_2 + 2e^- \longrightarrow 2\text{Cl}^-$	+1.35827
$\text{ClO}_4^- + \text{H}_2\text{O} + 2e^- \longrightarrow \text{ClO}_3^- + 2\text{OH}^-$	+0.36
$\text{ClO}_3^- + \text{H}_2\text{O} + 2e^- \longrightarrow \text{ClO}_2^- + 2\text{OH}^-$	+0.33
$\text{ClO}_2^- + \text{H}_2\text{O} + 2e^- \longrightarrow \text{ClO}^- + 2\text{OH}^-$	+0.66
$\text{ClO}^- + \text{H}_2\text{O} + 2e^- \longrightarrow \text{Cl}^- + 2\text{OH}^-$	+0.89
$\text{ClO}_4^- + 2\text{H}_3\text{O}^+ + 2e^- \longrightarrow \text{ClO}_3^- + 3\text{H}_2\text{O}$	+1.189
$\text{ClO}_3^- + 3\text{H}_3\text{O}^+ + 2e^- \longrightarrow \text{HClO}_2 + 4\text{H}_2\text{O}$	+1.21
$\text{HClO} + \text{H}_3\text{O}^+ + 2e^- \longrightarrow \text{Cl}^- + 2\text{H}_2\text{O}$	+1.482

Standard Electrode (Half-Cell) Potentials	
Half-Reaction	E° (V)
$\text{HClO} + \text{H}_3\text{O}^+ + \text{e}^- \longrightarrow \frac{1}{2}\text{Cl}_2 + 2\text{H}_2\text{O}$	+1.611
$\text{HClO}_2 + 2\text{H}_3\text{O}^+ + 2\text{e}^- \longrightarrow \text{HClO} + 3\text{H}_2\text{O}$	+1.628
$\text{Co}^{3+} + \text{e}^- \longrightarrow \text{Co}^{2+}$ (2 mol // H_2SO_4)	+1.83
$\text{Co}^{2+} + 2\text{e}^- \longrightarrow \text{Co}$	-0.28
$[\text{Co}(\text{NH}_3)_6]^{3+} + \text{e}^- \longrightarrow [\text{Co}(\text{NH}_3)_6]^{2+}$	+0.1
$\text{Co}(\text{OH})_3 + \text{e}^- \longrightarrow \text{Co}(\text{OH})_2 + \text{OH}^-$	+0.17
$\text{Cr}^3 + 3\text{e}^- \longrightarrow \text{Cr}$	-0.744
$\text{Cr}^{3+} + \text{e}^- \longrightarrow \text{Cr}^{2+}$	-0.407
$\text{Cr}^{2+} + 2\text{e}^- \longrightarrow \text{Cr}$	-0.913
$[\text{Cu}(\text{CN})_2]^- + \text{e}^- \longrightarrow \text{Cu} + 2\text{CN}^-$	-0.43
$\text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3\text{e}^- \longrightarrow \text{Cr}(\text{OH})_3 + 5\text{OH}^-$	-0.13
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}_3\text{O}^+ + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+} + 21\text{H}_2\text{O}$	+1.232
$[\text{Cr}(\text{OH})_4]^- + 3\text{e}^- \longrightarrow \text{Cr} + 4\text{OH}^-$	-1.2
$\text{Cr}(\text{OH})_3 + 3\text{e}^- \longrightarrow \text{Cr} + 3\text{OH}^-$	-1.48
$\text{Cu}^{2+} + \text{e}^- \longrightarrow \text{Cu}^+$	+0.153

Standard Electrode (Half-Cell) Potentials	
Half-Reaction	E° (V)
$\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$	+0.34
$\text{Cu}^+ + \text{e}^- \longrightarrow \text{Cu}$	+0.521
$\text{F}_2 + 2\text{e}^- \longrightarrow 2\text{F}^-$	+2.866
$\text{Fe}^{2+} + 2\text{e}^- \longrightarrow \text{Fe}$	−0.447
$\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+}$	+0.771
$[\text{Fe}(\text{CN})_6]^{3-} + \text{e}^- \longrightarrow [\text{Fe}(\text{CN})_6]^{4-}$	+0.36
$\text{Fe}(\text{OH})_2 + 2\text{e}^- \longrightarrow \text{Fe} + 2\text{OH}^-$	−0.88
$\text{FeS} + 2\text{e}^- \longrightarrow \text{Fe} + \text{S}^{2-}$	−1.01
$\text{Ga}^{3+} + 3\text{e}^- \longrightarrow \text{Ga}$	−0.549
$\text{Gd}^{3+} + 3\text{e}^- \longrightarrow \text{Gd}$	−2.279
$\frac{1}{2}\text{H}_2 + \text{e}^- \longrightarrow \text{H}^-$	−2.23
$2\text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{H}_2 + 2\text{OH}^-$	−0.8277
$\text{H}_2\text{O}_2 + 2\text{H}_3\text{O}^+ + 2\text{e}^- \longrightarrow 4\text{H}_2\text{O}$	+1.776
$2\text{H}_3\text{O}^+ + 2\text{e}^- \longrightarrow \text{H}_2 + 2\text{H}_2\text{O}$	0.00
$\text{HO}_2^- + \text{H}_2\text{O} + 2\text{e}^- \longrightarrow 3\text{OH}^-$	+0.878
$\text{Hf}^{4+} + 4\text{e}^- \longrightarrow \text{Hf}$	−1.55

Standard Electrode (Half-Cell) Potentials	
Half-Reaction	E° (V)
$\text{Hg}^{2+} + 2\text{e}^- \longrightarrow \text{Hg}$	+0.851
$2\text{Hg}^{2+} + 2\text{e}^- \longrightarrow \text{Hg}_2^{2+}$	+0.92
$\text{Hg}_2^{2+} + 2\text{e}^- \longrightarrow 2\text{Hg}$	+0.7973
$[\text{HgBr}_4]^{2-} + 2\text{e}^- \longrightarrow \text{Hg} + 4\text{Br}^-$	+0.21
$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Hg} + 2\text{Cl}^-$	+0.26808
$[\text{Hg}(\text{CN})_4]^{2-} + 2\text{e}^- \longrightarrow \text{Hg} + 4\text{CN}^-$	-0.37
$[\text{HgI}_4]^{2-} + 2\text{e}^- \longrightarrow \text{Hg} + 4\text{I}^-$	-0.04
$\text{HgS} + 2\text{e}^- \longrightarrow \text{Hg} + \text{S}^{2-}$	-0.70
$\text{I}_2 + 2\text{e}^- \longrightarrow 2\text{I}^-$	+0.5355
$\text{In}^{3+} + 3\text{e}^- \longrightarrow \text{In}$	-0.3382
$\text{K}^+ + \text{e}^- \longrightarrow \text{K}$	-2.931
$\text{La}^{3+} + 3\text{e}^- \longrightarrow \text{La}$	-2.52
$\text{Li}^+ + \text{e}^- \longrightarrow \text{Li}$	-3.04
$\text{Lu}^{3+} + 3\text{e}^- \longrightarrow \text{Lu}$	-2.28
$\text{Mg}^{2+} + 2\text{e}^- \longrightarrow \text{Mg}$	-2.372
$\text{Mn}^{2+} + 2\text{e}^- \longrightarrow \text{Mn}$	-1.185

Standard Electrode (Half-Cell) Potentials	
Half-Reaction	E° (V)
$\text{MnO}_2 + 2\text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{Mn}(\text{OH})_2 + 2\text{OH}^-$	-0.05
$\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \longrightarrow \text{MnO}_2 + 4\text{OH}^-$	+0.558
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \longrightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	+1.23
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.507
$\text{Na}^+ + \text{e}^- \longrightarrow \text{Na}$	-2.71
$\text{Nd}^{3+} + 3\text{e}^- \longrightarrow \text{Nd}$	-2.323
$\text{Ni}^{2+} + 2\text{e}^- \longrightarrow \text{Ni}$	-0.257
$[\text{Ni}(\text{NH}_3)_6]^{2+} + 2\text{e}^- \longrightarrow \text{Ni} + 6\text{NH}_3$	-0.49
$\text{NiO}_2 + 4\text{H}^+ + 2\text{e}^- \longrightarrow \text{Ni}^{2+} + 2\text{H}_2\text{O}$	+1.593
$\text{NiO}_2 + 2\text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{Ni}(\text{OH})_2 + 2\text{OH}^-$	+0.49
$\text{NiS} + 2\text{e}^- \longrightarrow \text{Ni} + \text{S}^{2-}$	+0.76
$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \longrightarrow \text{NO} + 2\text{H}_2\text{O}$	+0.957
$\text{NO}_3^- + 3\text{H}^+ + 2\text{e}^- \longrightarrow \text{HNO}_2 + \text{H}_2\text{O}$	+0.92
$\text{NO}_3^- + \text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{NO}_2^- + 2\text{OH}^-$	+0.10
$\text{Np}^{3+} + 3\text{e}^- \longrightarrow \text{Np}$	-1.856
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \longrightarrow 4\text{OH}^-$	+0.401

Standard Electrode (Half-Cell) Potentials	
Half-Reaction	E° (V)
$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2\text{O}_2$	+0.695
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}$	+1.229
$\text{Pb}^{2+} + 2\text{e}^- \longrightarrow \text{Pb}$	−0.1262
$\text{PbO}_2 + \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- \longrightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$	+1.69
$\text{PbS} + 2\text{e}^- \longrightarrow \text{Pb} + \text{S}^{2-}$	−0.95
$\text{PbSO}_4 + 2\text{e}^- \longrightarrow \text{Pb} + \text{SO}_4^{2-}$	−0.3505
$\text{Pd}^{2+} + 2\text{e}^- \longrightarrow \text{Pd}$	+0.987
$[\text{PdCl}_4]^{2-} + 2\text{e}^- \longrightarrow \text{Pd} + 4\text{Cl}^-$	+0.591
$\text{Pt}^{2+} + 2\text{e}^- \longrightarrow \text{Pt}$	+1.20
$[\text{PtBr}_4]^{2-} + 2\text{e}^- \longrightarrow \text{Pt} + 4\text{Br}^-$	+0.58
$[\text{PtCl}_4]^{2-} + 2\text{e}^- \longrightarrow \text{Pt} + 4\text{Cl}^-$	+0.755
$[\text{PtCl}_6]^{2-} + 2\text{e}^- \longrightarrow [\text{PtCl}_4]^{2-} + 2\text{Cl}^-$	+0.68
$\text{Pu}^3 + 3\text{e}^- \longrightarrow \text{Pu}$	−2.03
$\text{Ra}^{2+} + 2\text{e}^- \longrightarrow \text{Ra}$	−2.92
$\text{Rb}^+ + \text{e}^- \longrightarrow \text{Rb}$	−2.98
$[\text{RhCl}_6]^{3-} + 3\text{e}^- \longrightarrow \text{Rh} + 6\text{Cl}^-$	+0.44

Standard Electrode (Half-Cell) Potentials	
Half-Reaction	E° (V)
$\text{S} + 2\text{e}^- \longrightarrow \text{S}^{2-}$	-0.47627
$\text{S} + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2\text{S}$	+0.142
$\text{Sc}^{3+} + 3\text{e}^- \longrightarrow \text{Sc}$	-2.09
$\text{Se} + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2\text{Se}$	-0.399
$[\text{SiF}_6]^{2-} + 4\text{e}^- \longrightarrow \text{Si} + 6\text{F}^-$	-1.2
$\text{SiO}_3^{2-} + 3\text{H}_2\text{O} + 4\text{e}^- \longrightarrow \text{Si} + 6\text{OH}^-$	-1.697
$\text{SiO}_2 + 4\text{H}^+ + 4\text{e}^- \longrightarrow \text{Si} + 2\text{H}_2\text{O}$	-0.86
$\text{Sm}^{3+} + 3\text{e}^- \longrightarrow \text{Sm}$	-2.304
$\text{Sn}^{4+} + 2\text{e}^- \longrightarrow \text{Sn}^{2+}$	+0.151
$\text{Sn}^{2+} + 2\text{e}^- \longrightarrow \text{Sn}$	-0.1375
$[\text{SnF}_6]^{2-} + 4\text{e}^- \longrightarrow \text{Sn} + 6\text{F}^-$	-0.25
$\text{SnS} + 2\text{e}^- \longrightarrow \text{Sn} + \text{S}^{2-}$	-0.94
$\text{Sr}^{2+} + 2\text{e}^- \longrightarrow \text{Sr}$	-2.89
$\text{TeO}_2 + 4\text{H}^+ + 4\text{e}^- \longrightarrow \text{Te} + 2\text{H}_2\text{O}$	+0.593
$\text{Th}^{4+} + 4\text{e}^- \longrightarrow \text{Th}$	-1.90
$\text{Ti}^{2+} + 2\text{e}^- \longrightarrow \text{Ti}$	-1.630

Standard Electrode (Half-Cell) Potentials	
Half-Reaction	E° (V)
$\text{U}^{3+} + 3\text{e}^- \longrightarrow \text{U}$	-1.79
$\text{V}^{2+} + 2\text{e}^- \longrightarrow \text{V}$	-1.19
$\text{Y}^{3+} + 3\text{e}^- \longrightarrow \text{Y}$	-2.37
$\text{Zn}^{2+} + 2\text{e}^- \longrightarrow \text{Zn}$	-0.7618
$[\text{Zn}(\text{CN})_4]^{2-} + 2\text{e}^- \longrightarrow \text{Zn} + 4\text{CN}^-$	-1.26
$[\text{Zn}(\text{NH}_3)_4]^{2+} + 2\text{e}^- \longrightarrow \text{Zn} + 4\text{NH}_3$	-1.04
$\text{Zn}(\text{OH})_2 + 2\text{e}^- \longrightarrow \text{Zn} + 2\text{OH}^-$	-1.245
$[\text{Zn}(\text{OH})_4]^{2-} + 2\text{e}^- \longrightarrow \text{Zn} + 4\text{OH}^-$	-1.199
$\text{ZnS} + 2\text{e}^- \longrightarrow \text{Zn} + \text{S}^{2-}$	-1.40
$\text{Zr}^{4+} + 4\text{e}^- \longrightarrow \text{Zr}$	-1.539